Productivity Study of Cayuga Lake

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Abstract

This study aims to model productivity in Cayuga Lake based on aqueous carbon dioxide concentrations. Data was taken in July-September 2010 at varying depth at four locations near the outfall of the Ithaca Area Wastewater Treatment Facility and two reference locations. Carbon dioxide was measured using an OxyGuard Dissolved CO_2 meter and dissolved oxygen, chlorophyll, ammonium, and pH data were recorded with a Hydrolab DS 5. Titration techniques were used as a complimentary way to measure carbon dioxide concentration, as well as alkalinity. Three approaches were applied in the productivity analysis: simple carbon dioxide concentration differences over a diel period, dissolved oxygen concentration differences over a diel period, and carbon dioxide estimates based on ammonium ion concentrations. The third method proved most useful, yielding a strong relationship with the gathered CO_2 data. This method yielded a simple equation that allows for directly using CO_2 values measured by the OxyGuard meter as an estimate of productivity.

Acknowledgements

This research project was made possible by Jose Lozano, Director of the Environmental Laboratory at the Ithaca Area Waste Water Treatment Facility and my mentor while I interned there. He provided the material and intellectual basis and his advice and guidance have been invaluable. Todd Walter, Professor of Biological and Environmental Engineering at Cornell University and my Master's thesis advisor, empowered me and gave me academic freedom to pursue this project.

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Productivity Study of Cayuga Lake

1) Background

This project was undertaken with the intention of modeling the metabolic state of Cayuga Lake in upstate New York. The project was performed in conjunction with the Ithaca Area Waste Water Treatment Facility in Ithaca NY, where I acted as an intern under the supervision of Jose Lozano from June - November 2010. In order to perform the analysis, aqueous carbon dioxide readings as well as a host of other data (pH, chlorophyll, and dissolved oxygen among others) were taken at varying depths at pre-selected locations in the vicinity of the wastewater treatment plant outfall. Data considered in the analyses lie in the time range of July 27 - September 21, 2010. Topical background information follows.

The carbonate system acts to control the pH of many marine environments, including our site of interest, Cayuga Lake. This system is comprised of $CO_{2\,(aq)}$, H_2CO_3, HCO_3^-, and CO_3^{2-}. Acidic waters see CO_2 and H_2CO_3 as the dominant species, while higher concentrations of CO_3^{2-} are indicative of strongly basic waters. Bodies of water in the pH range of approximately 6.3-10.3 are characterized by high concentrations of HCO_3^- in relation to the other species. Figure 1 presents the distribution of carbonate species over a range of pH. Note the log concentration scale, indicating a 10-fold decrease in concentration from -2 to -3, a 100-fold decrease from -2 to -4, etc.

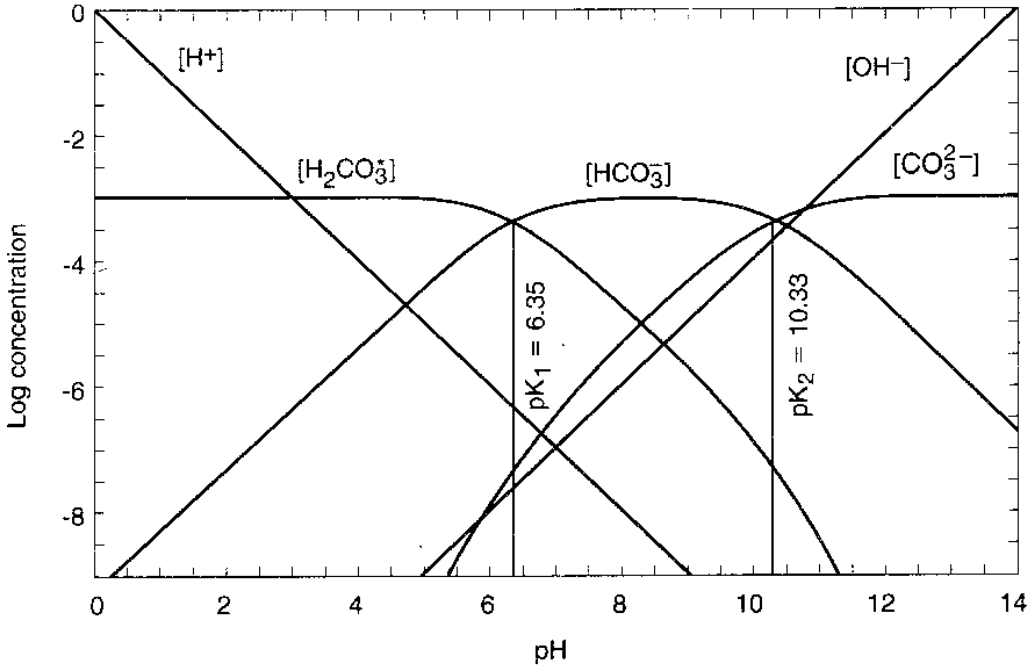


Figure 1. Log-concentration vs. pH for the carbonate system (Metcalf & Eddy 1755).

It is difficult to differentiate between $CO_{2\,(aq)}$ and H_2CO_3 and their combined concentrations are often represented as a new species, $H_2CO_3^*$. This theoretical substance is comprised overwhelmingly (more than 99.85%) by dissolved carbon dioxide and is used as a convenience in calculations. Detailed equilibria methodology is given in Appendix 1.

Total Carbonates (C_T) = $[H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$ (Appendix 1, eq. 1)

The alkalinity of a water is its capacity to neutralize acid. It is based on the same carbonate species mentioned above, but takes into account their ionization level. HCO_3^- can neutralize one proton before becoming a neutral species and ceasing to contribute to alkalinity. By similar logic, CO_3^{2-} neutralizes two protons and therefore contributes to alkalinity twice as strongly as HCO_3^-. Water itself contributes to alkalinity by dissociating to its H^+ and OH^- ions. Hydroxide contributes one unit to alkalinity, while H^+ represents a generic acidifying species and therefore can be represented as negative alkalinity.

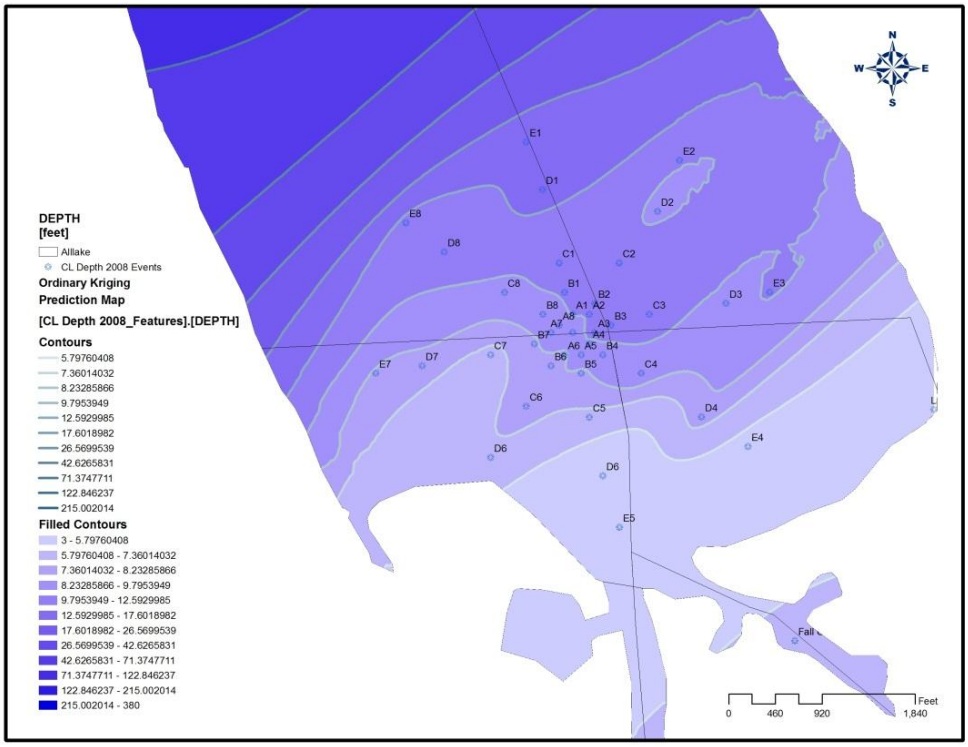
Alkalinity (Alk) = $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$ (Appendix 1, eq. 18)

Our site of study is Cayuga Lake, one of the Finger Lakes in upstate New York. The lake is long and narrow and exhibits longitudinal stratification of depth, with the south end of the lake much shallower than the north; the deepest point in the lake is 433 ft, while the south end is on average 10ft in depth.

The study focused on the idea that CO_2 levels would vary with diel cycles in the lake and could therefore be used as indicators of productivity levels at varying depth. Theoretically, lower CO_2 levels should be observed in the shallower south end of Cayuga Lake because sunlight sufficiently penetrates to the bottom, enabling submergent macrophytes to take root. These act in conjunction with algae to deplete aqueous carbon dioxide during the process of photosynthesis.

Another central point in the study is that because CO_2 levels vary throughout the day, maximum levels should theoretically occur just before dawn. This is because photosynthetic activity ceases after sunset but respiration continues, creating CO_2 as a by-product that cannot be used by photosynthetic organisms until the next sunrise.

Readings were taken in the early morning and in late afternoon at varying depths to reflect these factors. Locations of sampling sites and measurement depths are summarized in Table 1 and Figure 2 shows their relative locations. The intersection at the center of Figure 2 represents the wastewater treatment plant outfall location.



Location	Depth (ft)
Inlet	5
E2	5
E3	7
E8	7
RUSS	10
RUSS	20
Crowbar Point	10
Crowbar Point	20

Figure 2 and Table 1. Spatial locations of sampling sites and corresponding specific sampling depths.

2) Methods

The study aimed to measure dissolved carbon dioxide levels as an indicator of lake productivity. Because Cayuga Lake has a slightly basic pH (~8.2), most of the carbon exists in the HCO_3^- form. An OxyGuard Dissolved CO_2 meter was used to measure carbon dioxide. This necessitated lowering the pH of the samples down to a pH range of 3-4, where the dominant carbonate system species would be CO_2 (see Figure 1); the analyzer then gives a CO_2 reading representative of total carbonates. pH was lowered by adding 1 gram of citric acid crystals to the samples and immediately stirring in order to dissolve the crystals.

There were concerns about some CO_2 escaping to the atmosphere during the stirring process; these losses were minimized by stirring in a well-sealed electrode chamber for only a few seconds before measurement. Also, carbon dioxide is highly soluble in water and has a relatively low affinity for escaping into the gaseous phase, according to Henry's Law. It is impossible to measure the precise amount of dissolved CO_2 that may have volatilized to the atmosphere before measuring, but the amount was likely low enough to be considered insignificant.

Henry's Law: $K_H P_{CO2} = C_T \alpha_o$ (Appendix 1, eq. 18)

In the above, K_H is the Henry's Law constant for carbon dioxide, assumed to be 0.034 mol/L-atm. α_o stands for the fraction of carbonates present as carbon dioxide. The partial pressure of carbon dioxide, P_{CO2}, was found by augmenting atmospheric pressure data from the weather station at the Ithaca Area Waste Water Treatment Facility (IAWWTF). This weather station has been operational since June 2010 and data is monitored and stored by Nathaniel Carman, intern at the wastewater facility. The weather station and facility are located near the south end of Cayuga Lake and readings taken at that site are assumed to be accurate for analysis of the sample data. Pressure is recorded every ten minutes, and wind data once per minute. The pressure reading taken closest to the time of sampling was used in calculations. Atmospheric pressure data is converted from millimeters of mercury (mmHg) to atmospheres (atm), and the partial pressure of CO_2 (P_{CO2}) is taken to be 0.033% of atmospheric pressure (Cole 183).

Samples were taken at different points in the day, specifically near dawn (between the hours of 3AM and 7AM) and late afternoon to emphasize different photosynthetic activities. Before dawn, macrophytes and algae in the lake are unable to photosynthesize but other organisms are still respiring; these factors combine to produce the highest theoretical daily dissolved CO_2 levels. By afternoon, photosynthesis is again occurring and one can expect lower dissolved CO_2 readings than observed at dawn.

Equipment used included a Masterflex E/S Portable Sampler, an OxyGuard CO_2 Analyzer, and a Hydrolab DS5 (see figure 3). The CO_2 analyzer measures only dissolved carbon dioxide, not total carbonates. As noted above, Cayuga Lake's pH of ~8.2 means a majority of carbonates are present as bicarbonate. To overcome this, citric acid is added to the samples to bring the pH to a level where the majority of carbonates would be present as CO_2 and the machine would be able to detect a reading. The CO_2 analyzer is a relatively new machine and its accuracy has been disputed; however, a study by Moran concluded that the device is "useful in situations where accurate pH and carbonate alkalinity determinations are difficult to obtain," with an accuracy of ±1mg/L. The meter has faster response times with increasing water velocity; more specifically, "the time to 95% span was less than 10min at water velocities of 9cm/s and above." For the purposes of this study, the stirring action of the meter is assumed to bring the sample to a high enough velocity for the response time to be adequate for accurate CO_2 readings.

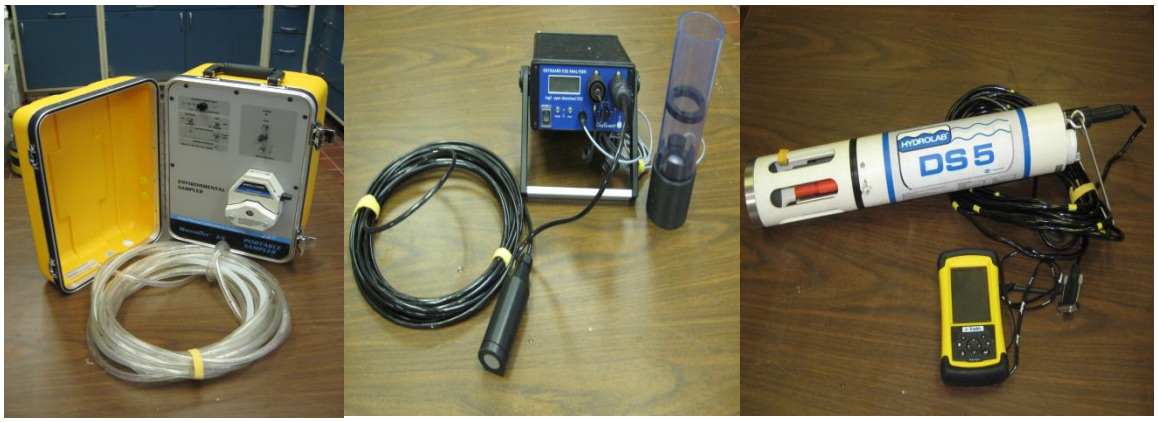


Figure 3. Portable sampler, CO2 analyzer, and Hydrolab used in the study.

500mL samples for lab analysis were immediately placed inside a dark, ice-filled cooler to prevent photosynthetic use of CO_2 before we could measure its level. In addition, 200mL samples were treated with citric acid in order to measure CO_2 levels directly at the sampling sites. pH paper strips were used as an approximate measure of the solution's pH after addition of citric acid. All pH readings were in the 2-3 range, where the overwhelming majority of carbonates are present as carbon dioxide. These CO_2 readings were assumed to be an accurate measure of total carbonates in calculations. This allowed the determination of the fraction of total carbonates contributed by the conversion of bicarbonate to carbon dioxide when pH was augmented with citric acid. Subtracting this fraction from the total carbonates yields the initial dissolved CO_2 levels.

Upon arrival at the lab, the 500mL samples were promptly analyzed to see if dissolved CO_2 levels were comparable to those measured on the lake. Alkalinity of the samples was also measured. Titration with phenolphthalein and NaOH was used to determine the amount of aqueous CO_2. Bromcresol green and sulfuric acid titrations were used to determine the alkalinity of the samples. These tests follow the guidelines presented by the "Standard Methods for the Examination of Water and Sewage," as modified by Welch (Welch 213-216) and summarized below.

To measure CO_2, ten drops of phenolphthalein indicator are added to 100 mL of the sample water and titrated with N/44 NaOH solution. The amount of free aqueous CO_2 in parts per million is found by multiplying the volume of NaOH used in titration by ten.

Alkalinity is expressed in two parts, phenolphthalein alkalinity and methyl orange alkalinity. Phenolphthalein alkalinity represents alkalinity in the pH range of 8.3 – 10.0 (Gossett, "Alkalinity and Acidity" 7); this alkalinity is mostly due to carbonate (CO_3^{2-}), the dominant species at basic pH. To measure phenolphthalein alkalinity, four drops of the indicator are added to a 100 mL volume of sample and titrated with sulfuric acid. The phenolphthalein alkalinity is expressed as ten times the volume of sulfuric acid added.

Methyl orange alkalinity approximately measures the alkalinity in the pH range of 4.3-8.2, where bicarbonate (HCO_3^-) is dominant. Bromcresol green indicator has a similar

turning point as methyl orange and was used as a replacement because its turning point was easier to see. In order to measure the methyl orange alkalinity, 8 drops of bromcresol green were added to a fresh 100 mL volume of sample and titrated with sulfuric acid. The methyl orange alkalinity is equal to 10 times the volume of sulfuric acid added.

Total alkalinities resulting from the different carbonate species are given by a table presented by the "Standard Methods for the Examination of Water and Sewage," modified by Welch and reprinted below.

Result of Titration	Alkalinities Expressed as P.P.M. of Calcium Carbonate		
	Hydroxide	Carbonate	Bicarbonate
P = 0	0	0	T X 10
P < ½ T	0	2P X 10	(T – 2P) X 10
P = ½ T	0	2P X 10	0
P > ½ T	(2P – T) X 10	2(T – P) X 10	0
P = T	T X 10	0	0

Table 2. Results of Titration and Alkalinities. Taken from "Limnological Methods," Welch 215.

In the above, P represents the volume of H_2SO_4 used in the phenolphthalein titration and T represents the total volume of H_2SO_4 used in both titrations. The titrations fell in the "P < ½ T" category and the corresponding alkalinity equations were used to find carbonate and bicarbonate concentrations (see Appendix 2).

The CO_2 levels found by titration with NaOH in lab are much lower than those measured on the lake. This disparity is caused by the need to lower sample pH with citric acid in order to be able to measure dissolved CO_2; this converts bicarbonate to carbon dioxide and creates artificially high CO_2 readings. To correct for this, equations 13, 14, and 15 in Appendix 1 were used to ascertain the different carbonate species as fractions of total carbonates at the original lake pH and at the artificially lowered pH. The reduction of bicarbonate levels in the conversion to a lower pH represents an equal increase in the CO_2 concentration. The actual CO_2 level is found by subtracting the fraction of bicarbonate from the artificially high CO_2 reading. Example calculations are included as Appendix 2.

Three relationships were analyzed to gain an understanding of lake productivity based on carbon dioxide and oxygen data. As a preliminary method, the difference in CO_2 concentrations (found by the method in Appendix 1) between close day/night sampling date pairs was used as an estimate of productivity.

The second estimation method is based on oxygen concentration differences. Cole et.al. define Net Ecosystem Productivity (NEP) by the following relationship:

$\Delta O_2 = NEP + D$

where D represents the diffusive oxygen exchange with the atmosphere and O_2 is the measured oxygen concentration in water (Cole 1720). D is defined as a function of wind speed:

$D = k(O_2 - O_{2\,sat})$

Wind speed data was taken from the wastewater treatment plant weather station. This data is logged every minute, so wind speeds were available for the exact time when samples were taken.

The transfer coefficient k is the variable that is dependent on wind speed, V_{wind}, which must be expressed in terms of in m/s. MacIntyre et.al. define k as:

$\ln(k) = 1.09 + 0.249 * V_{wind}$

Wind effects are assumed to only be significant at the water surface, so the variable D is included in only the surface samples. The other NEP values at lower depths are assumed to be due solely to the change in oxygen concentrations between sampling day/night pairs.

The third measure of productivity was based on the idea that productivity levels must be corrected for carbon stored in the $NH_4HCO_3^-$ compound. The sum of CO_2 stored as HCO_3^-, CO_3^{2-} , and aqueous CO_2 is then an estimate of lake metabolism. The method was first proposed by Ohle in 1956. Appendix 3 outlines the calculations, as presented by Wetzel and Likens 1991.

This estimate of productivity was mapped against the original dissolved CO_2 readings taken by the OxyGuard meter (the values were not augmented to account for the bicarbonate and carbonate that were now converted to CO_2) to arrive at a simple linear relationship between carbon dioxide readings and lake productivity. This method is the simplest for estimation of metabolism, as it requires no mathematical analysis of the readings given by the meter other than using a simple, univariate formula.

3) Results and Analysis

Aqueous Carbon Dioxide Measurement Accuracy – Titration vs. Theoretical Values

Data on p. 12-13 represents sampling done at dawn on July 27, August 11, August 17, and September 21, 2010 and in the afternoon on July 28, August 16, and September 14, 2010. The carbon dioxide levels were found by two methods: titration and analytically by methods discussed above and presented in Appendix 1.

Figures 4-7 represent samples taken at dawn and Figures 8-10 samples taken in the afternoon. The two CO_2 measurement methods discussed give all-around positive results, with correlations of 0.909, 0.999, 0.985, and 0.976 for the AM samples and 0.910 and 0.993 for two of the PM samples.

For the third set of PM samples (Figure 8, July 28), the titrated CO_2 readings were all zero; that is, upon addition of phenolphthalein indicator to the samples, a faint pink color appeared even before addition of any sodium hydroxide. Since the free carbon dioxide is calculated by multiplying the volume of NaOH added by ten (see methods), the CO_2 levels are zero by default by the titration method. This result is actually encouraging, because the July 28 readings were taken at mid-day when CO_2 levels are expected to be lower than in the early morning due to photosynthetic uptake. Because titration is an approximate process, any dissolved CO_2 in the July 28 samples was likely insignificant – most carbonates were likely present as bicarbonate, HCO_3^- (See figure 1 – the dominant species at Cayuga Lake's pH of ~8.2 is bicarbonate).

The second data point in the "theoretical" series on August 16 (Figure 9) is missing because of a failure to record pH when sampling and a subsequent inability to perform the necessary calculations.

Correlation was above 0.9 for all other sampling dates, both AM and PM, leading to the conclusion that addition of citric acid to the samples in order to analytically calculate the aqueous CO_2 content does not significantly alter the true concentrations; therefore, this method is a viable alternative to titration.

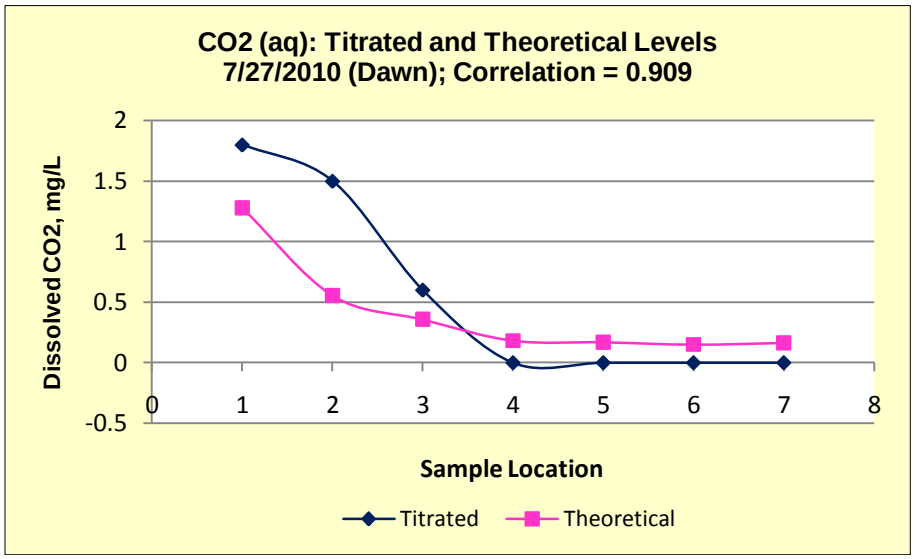


Figure 4

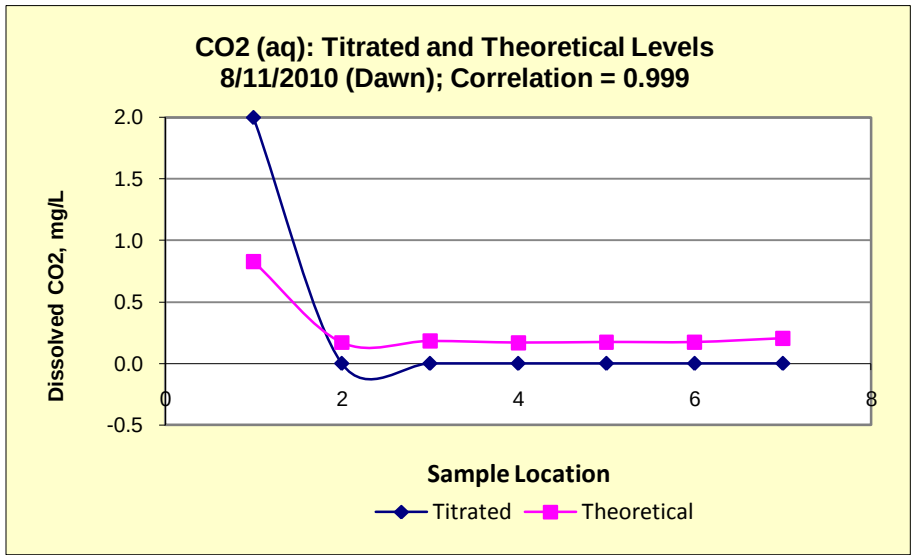


Figure 5

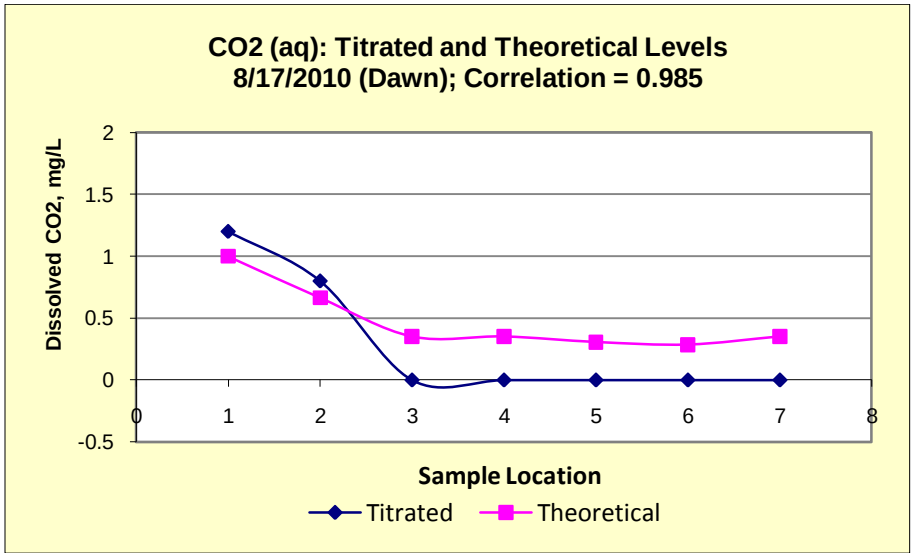


Figure 6

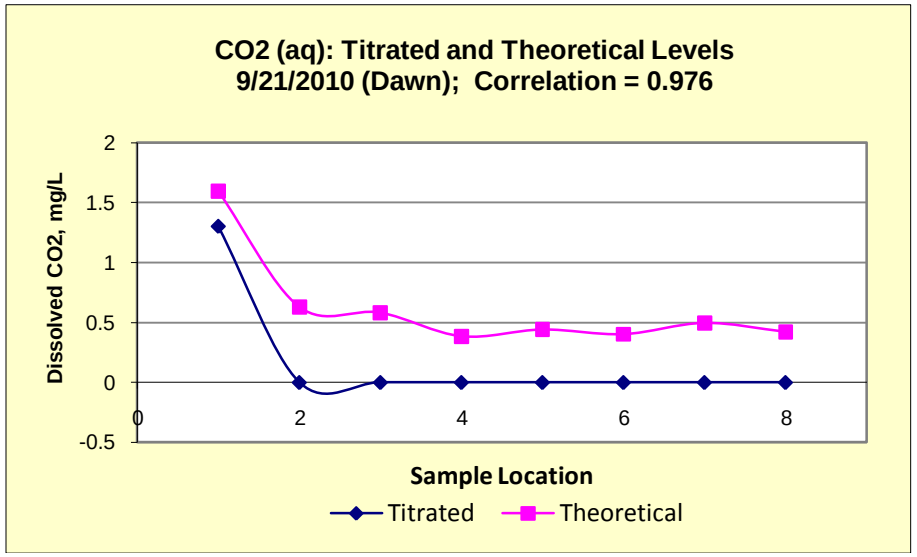


Figure 7

Figures 4-7. CO_2 measured by titration and by calculation, AM samples.

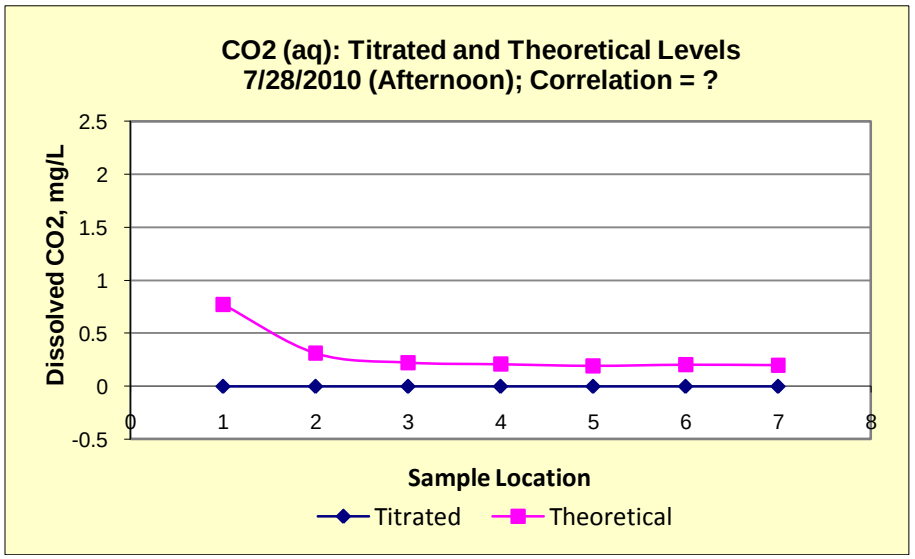


Figure 8

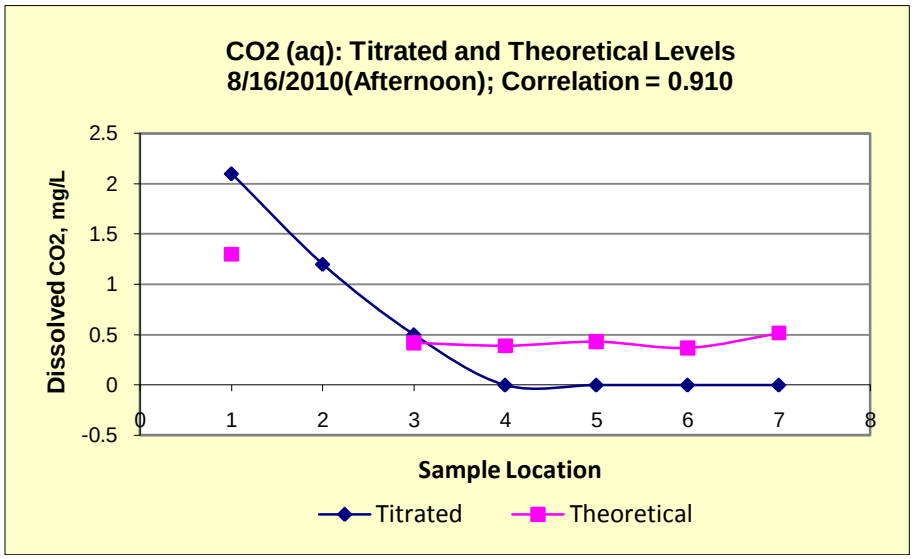


Figure 9

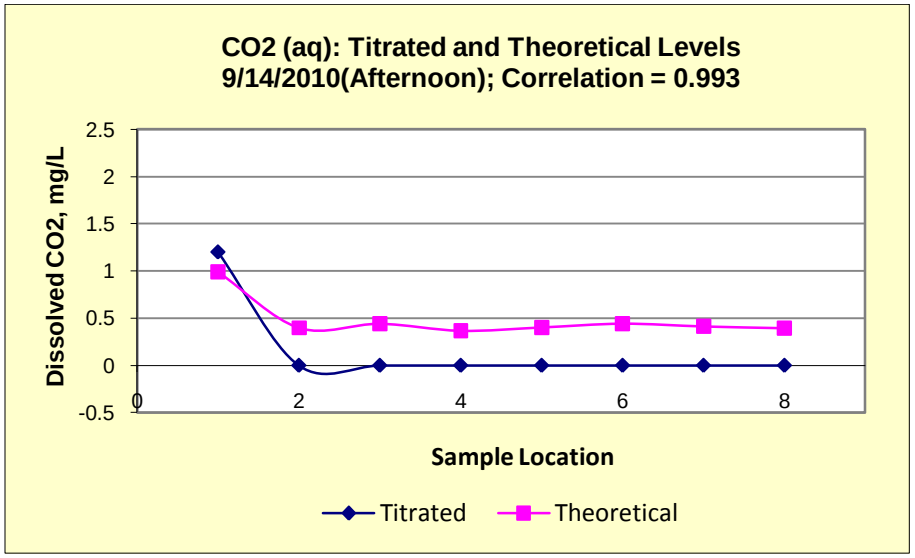


Figure 10

Figures 8-10. CO_2 measured by titration and by calculation, PM samples.

Alkalinity – Titration vs. Theoretical Values

Dawn alkalinity results were promising, with titrated and calculated values correlating at over 92% for the June 27 and August 11 sampling dates (Figures 8-9). The correlation was much lower for the August 17 samples; this could possibly be attributed to the imprecision of the titration technique. Titrated values seem to be slightly higher than the mathematically predicted values in most cases, but both methods follow the same trend: higher alkalinity at the inlet, then a tapering towards 100 mg/L at the other sampling sites. Alkalinity is a conserved value because neither the partial pressure of CO_2 nor the concentration of H_2CO_3 in water is involved in charge balance (Appendix 1, eq. 18), as they are uncharged species (Drever). The alkalinity measurements indicate this – the alkalinity values are similar in magnitude for both early morning and mid-day samples.

Alkalinity found by titration and by mathematical analysis yielded very similar values for the afternoon samples, with July 28 and August 16 agreeing at 96%. Again, this is expected because alkalinity is a conserved value that should not vary over a diel period. As with the dawn samples, the alkalinity values are highest at the inlet and then taper to about 100 mg/L at the other locations.

Correlation between titration and theoretical alkalinity values was slightly lower on Sept. 21 and Sept. 14 (Figures 14 and 17). This is could be due to a variety of factors (instrument measurement accuracy, human error etc) but the most likely cause of lower correlation is the inaccuracy of the titration technique. Because one is looking for a color change to indicate the turning point of the titration, an extra drop of acid when unsure of the correct magnitude of color change can skew the alkalinity results greatly. The theoretical, mathematically derived alkalinity values may be more trustworthy in terms of number value, but both methods follow roughly the same trends; this is indicative of the applicability of both methods in finding of alkalinity.

In many of the sampling points, the titrated alkalinities were higher in magnitude than the calculated values. This leads to the conclusion acid was probably added beyond the methyl orange and phenolphthalein turning points due to human error, ie not being able to correctly discern the subtle color changes for the indicators.

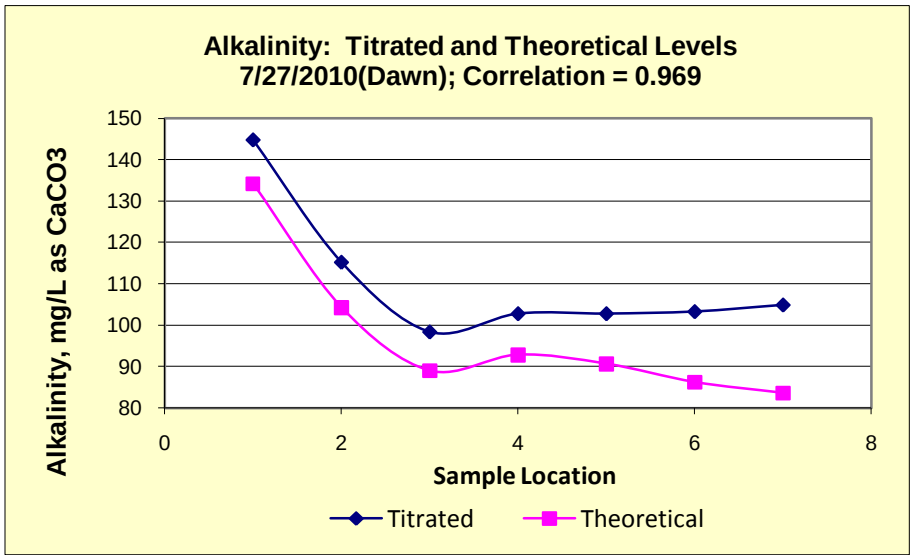


Figure 11

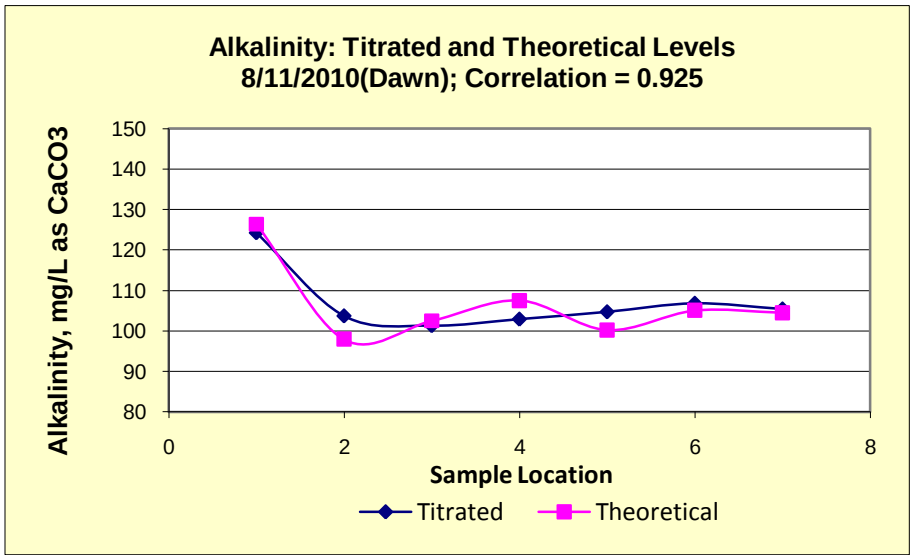


Figure 12

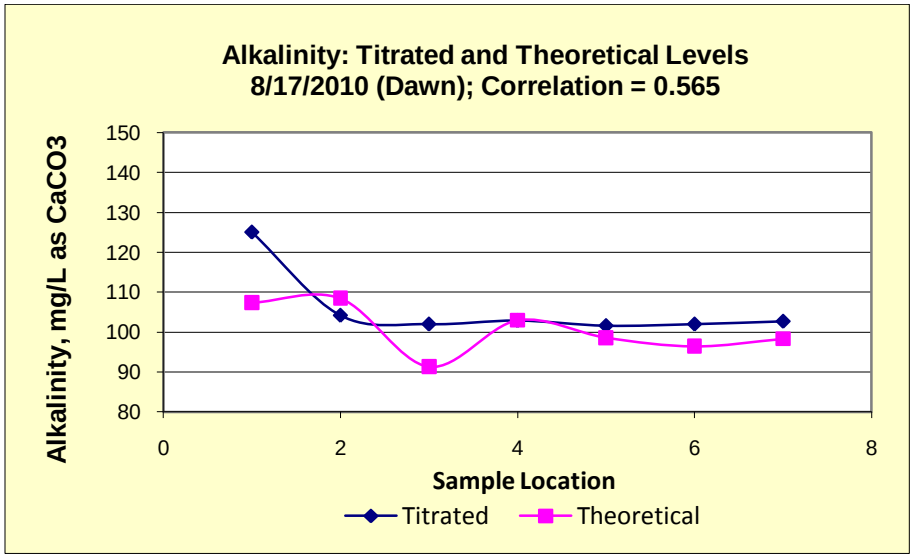


Figure 13

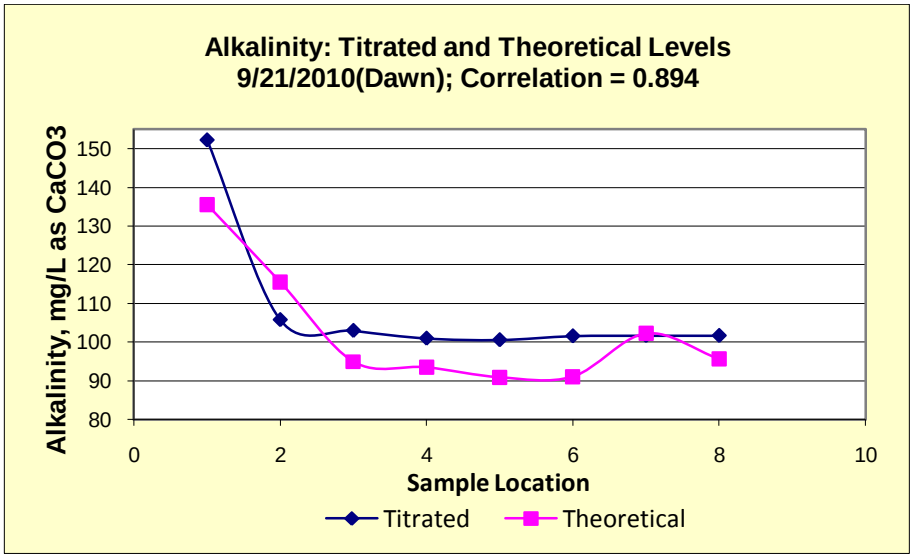


Figure 14

Figures 11-14. Alkalinity measured by titration and by calculation, AM samples

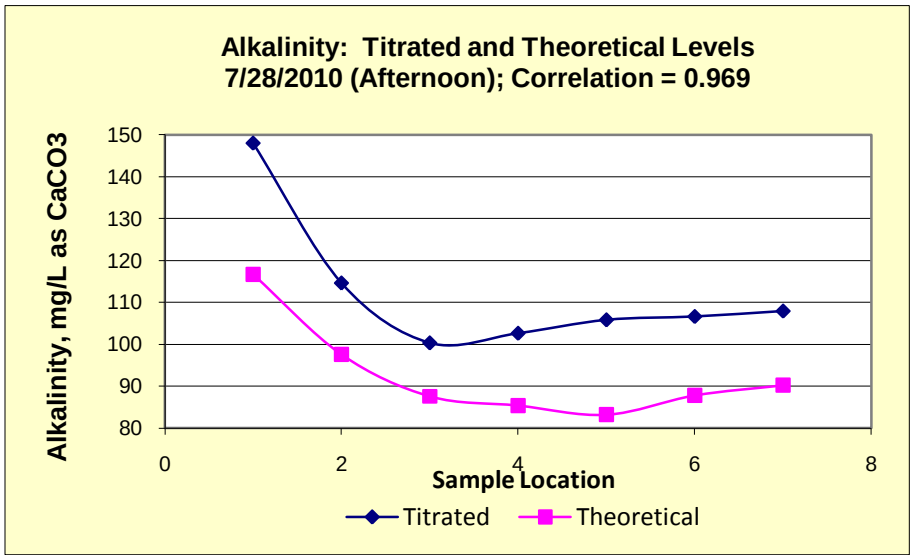


Figure 15

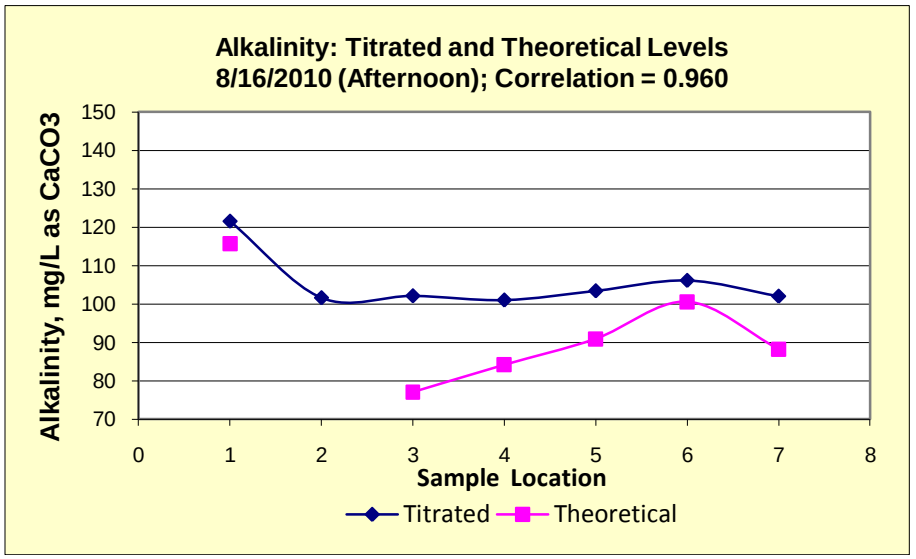


Figure 16

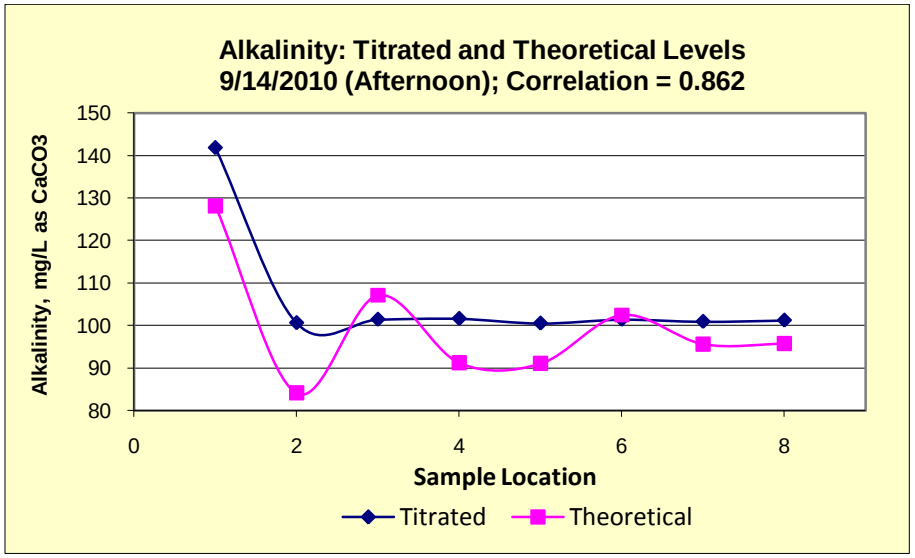


Figure 17

Figures 15-17. Alkalinity measured by titration and by calculation, PM samples.

Aqueous Carbon Dioxide as Fraction of Total Carbonates

Dissolved CO_2 values measured with the OxyGuard CO_2 analyzer were artificially high because pH needed to be augmented with citric acid to take these readings. These carbon dioxide levels detected by the analyzer in fact represent *all* carbonates present in the sample water.

Location	Average Percent CO_2 (CO_2/C_T * 100)	
	AM Samples	PM Samples
Inlet	1.90	2.01
E2	-	1.07
E3	1.00	0.36
E8	0.73	0.91
RUSS (10ft)	0.53	0.81
Crowbar Point (10ft)	0.52	0.81
RUSS (20ft)	0.49	0.69
Crowbar Point (20ft)	0.58	0.92

Table 3. Average Percent Aqueous Carbon Dioxide, as Presented by Figures 18-24.

Some freshwater macrophytes are able to use both CO_2 and HCO_3^- for photosynthesis. Macrophytes that are only able to use CO_2 are found to have a higher affinity for its uptake than those species that can use both carbon sources, where affinity is calculated as the slope of net photosynthetic rate against CO_2 concentration (Maberly and Madsen).

Species distribution is related to alkalinity and pH of the water, with higher pH waters such as Cayuga Lake containing macrophyte species that are able to use bicarbonate as their carbon source (although CO_2 seems to be the preferable carbon source). The exact species distribution in Cayuga Lake was beyond the scope of this project, but is likely dominated by species that can use bicarbonate for photosynthesis because this is the most dominant carbonate species at the lake's pH of ~8.

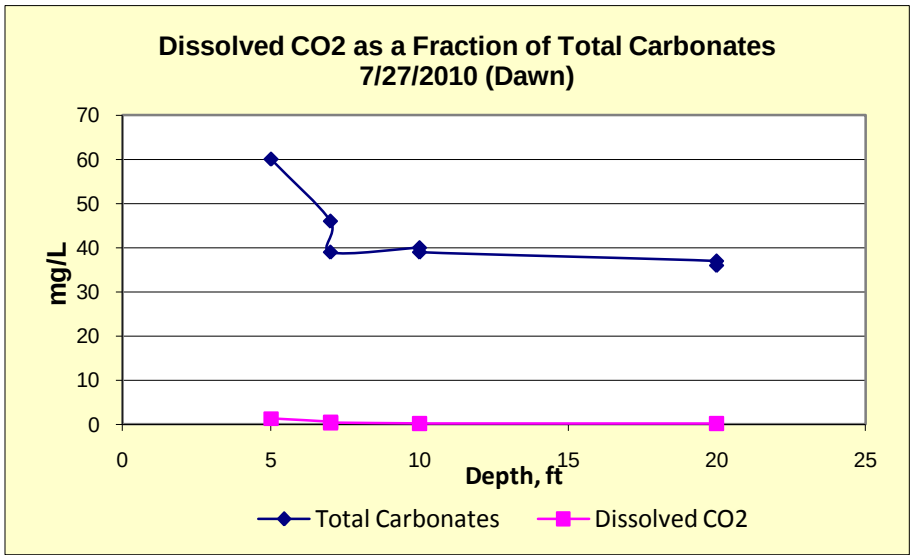
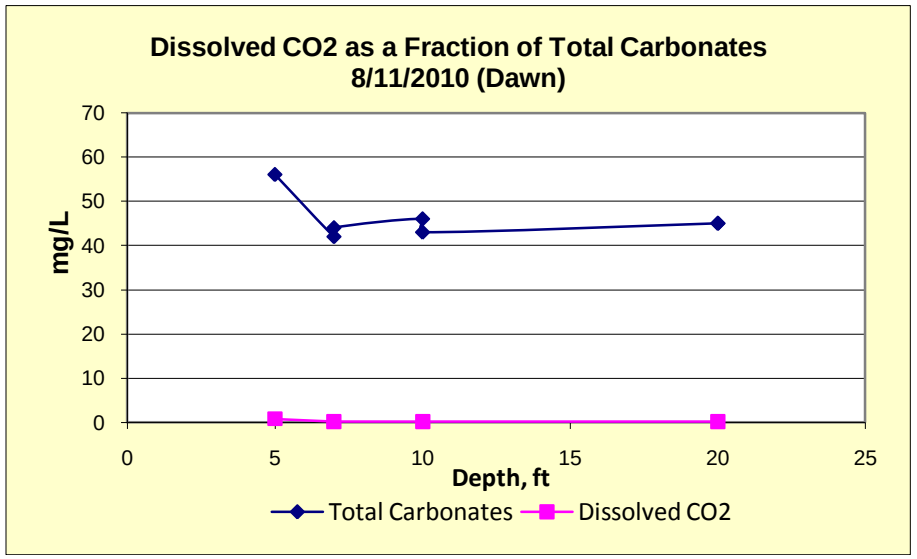


Figure 18



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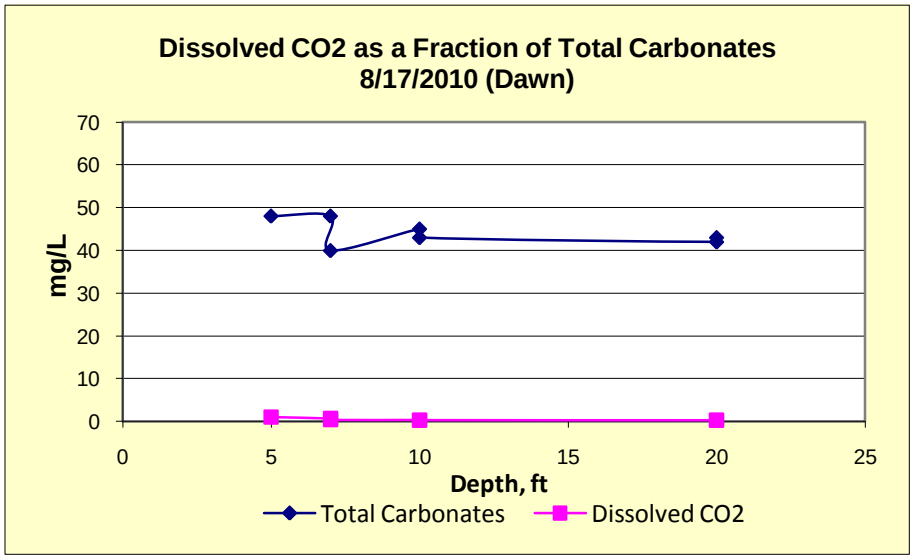

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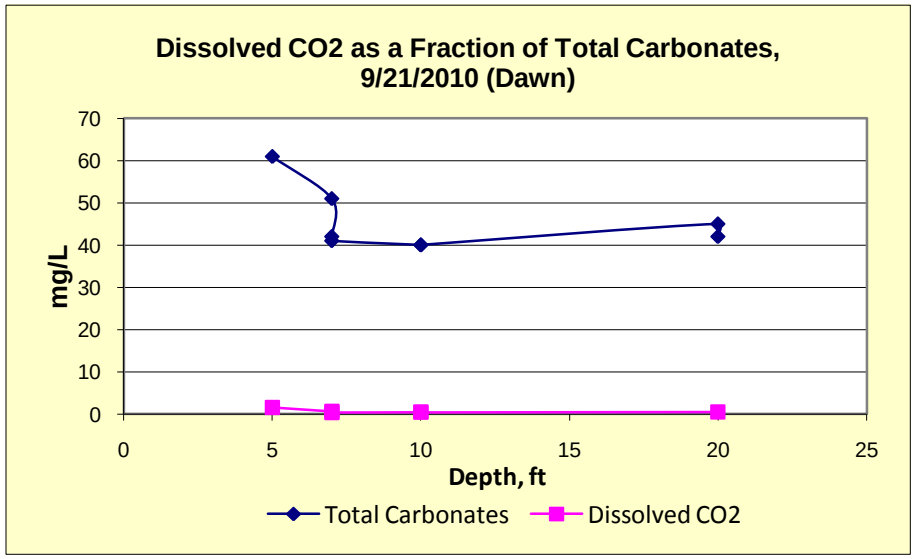
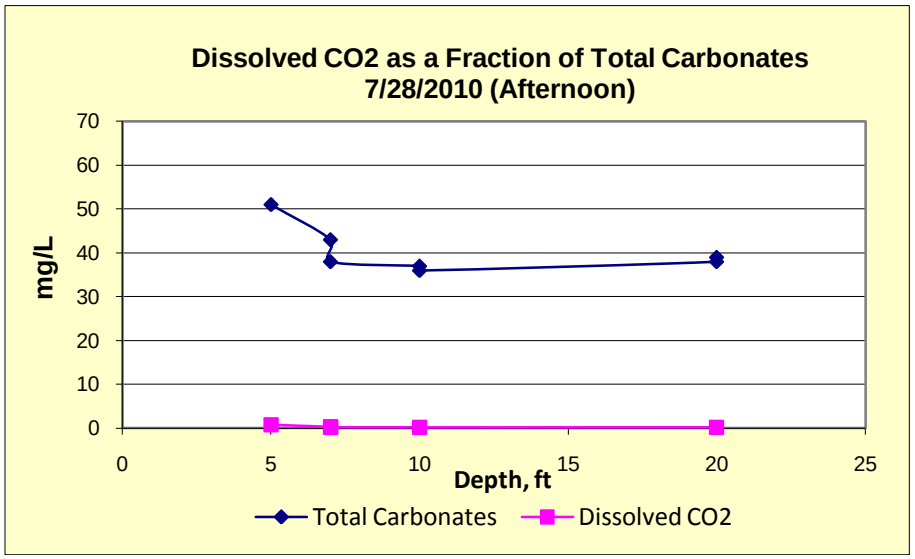


Figure 21

Figures 18-21. Aqueous Carbon Dioxide as a Calculated Fraction of Total Carbonates, AM samples.



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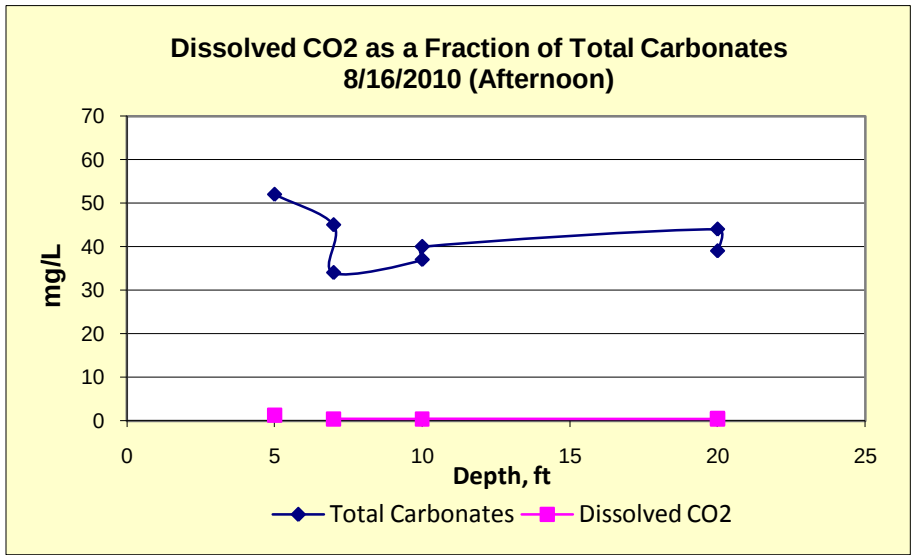


Figure 23

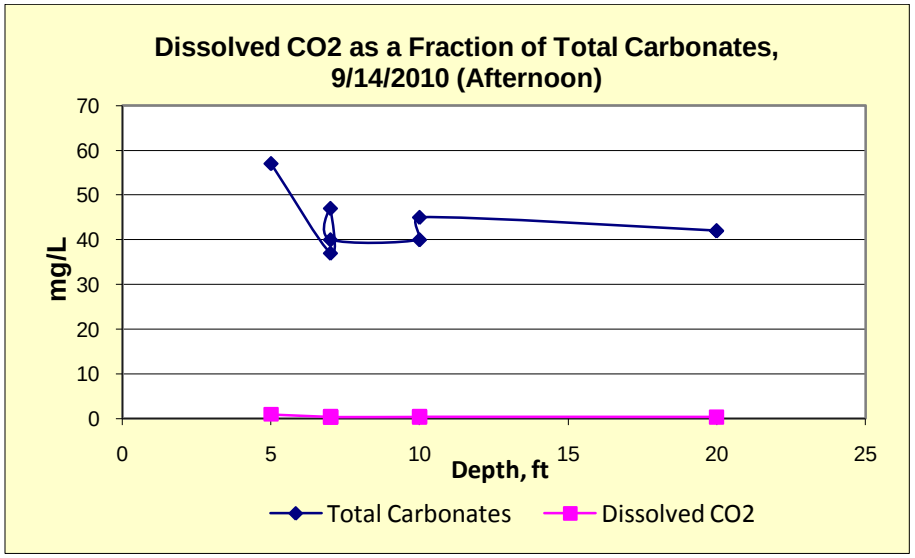
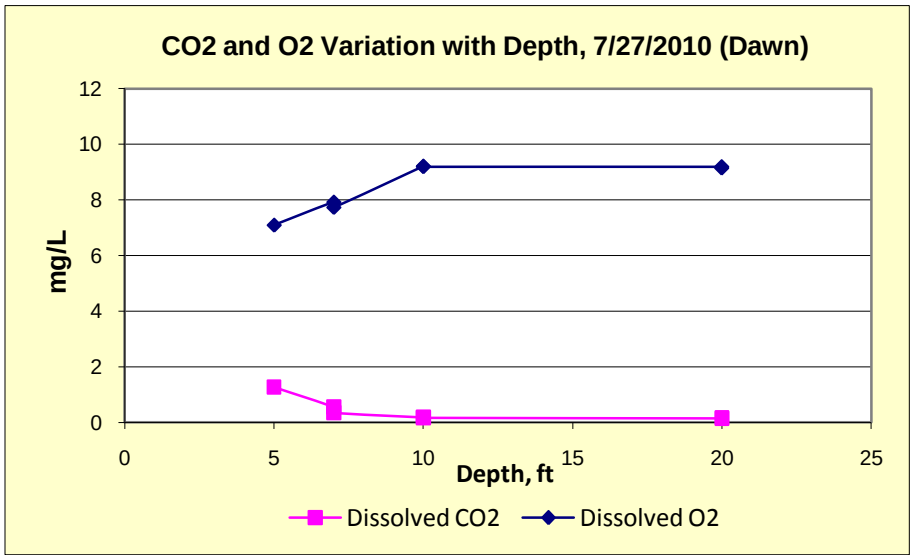


Figure 24

Figures 22-24. Aqueous Carbon Dioxide as a Calculated Fraction of Total Carbonates, PM samples.

Aqueous Carbon Dioxide and Oxygen Variation with Depth

Carbon dioxide and oxygen levels vary inversely with depth, as expected. The most marked inverse relationship seems to be at depths shallower than 10 ft, with both CO_2 and O_2 concentrations leveling off at greater depths. These results are expected because macrophytes and algae are most active in the 0-10 ft depth range where sunlight penetration is sufficient for photosynthesis to occur, and the lake is shallow enough to allow macrophytes to take root.



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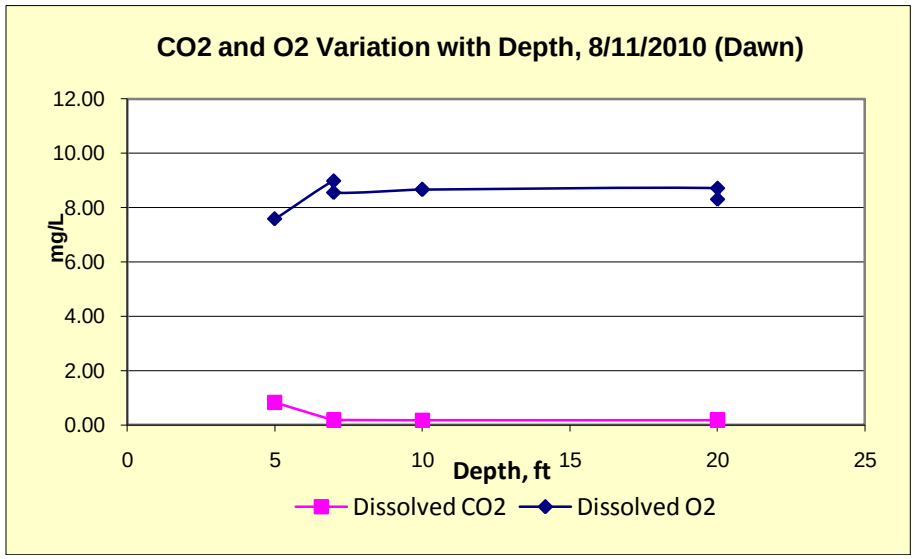

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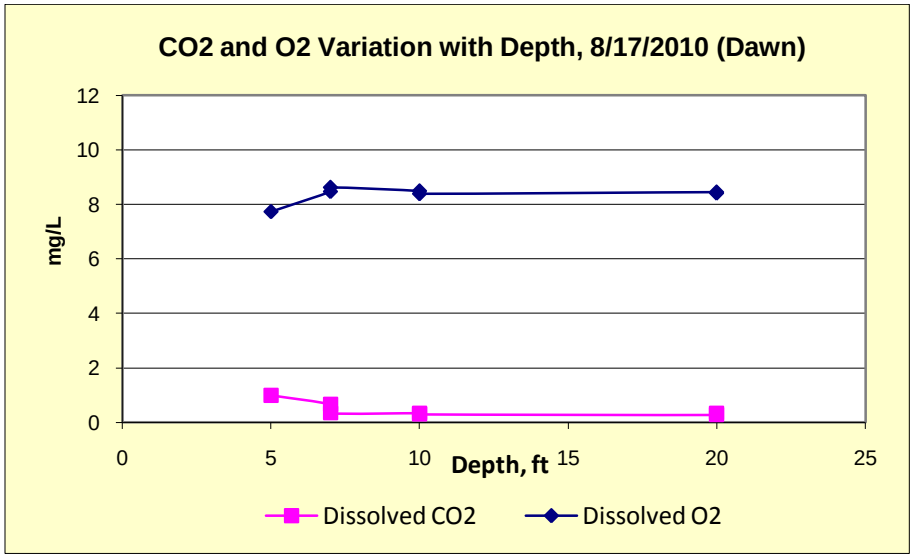


Figure 27

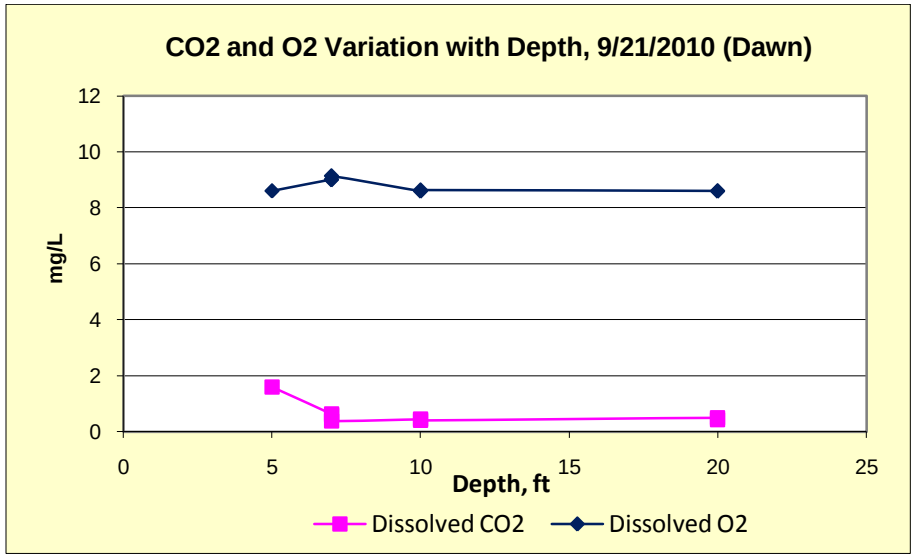


Figure 28

Figures 25-28. Inverse Relationship Between Aqueous Carbon Dioxide and Oxygen Levels, AM Samples.

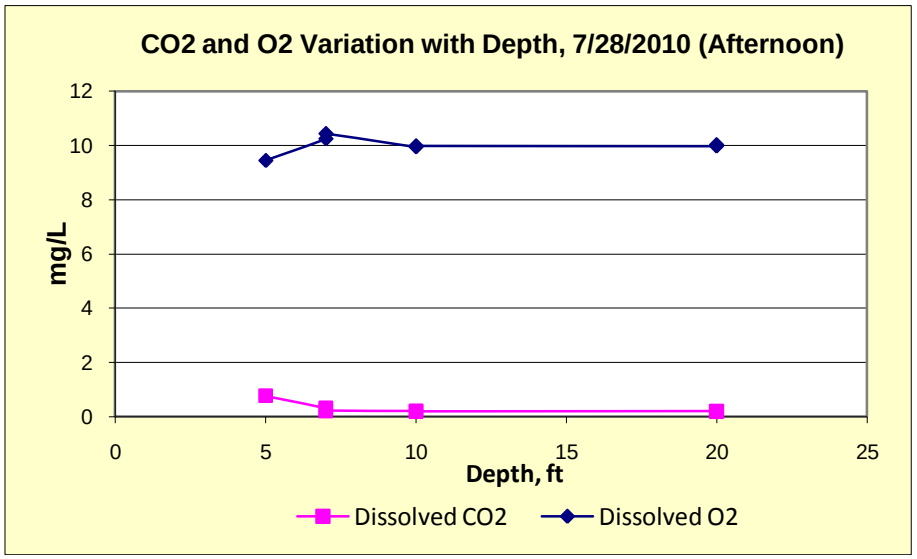
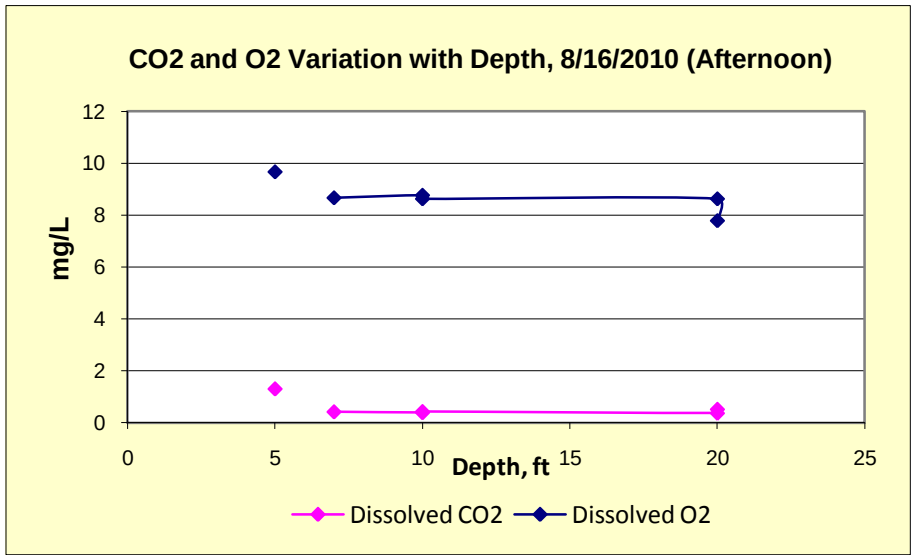


Figure 29



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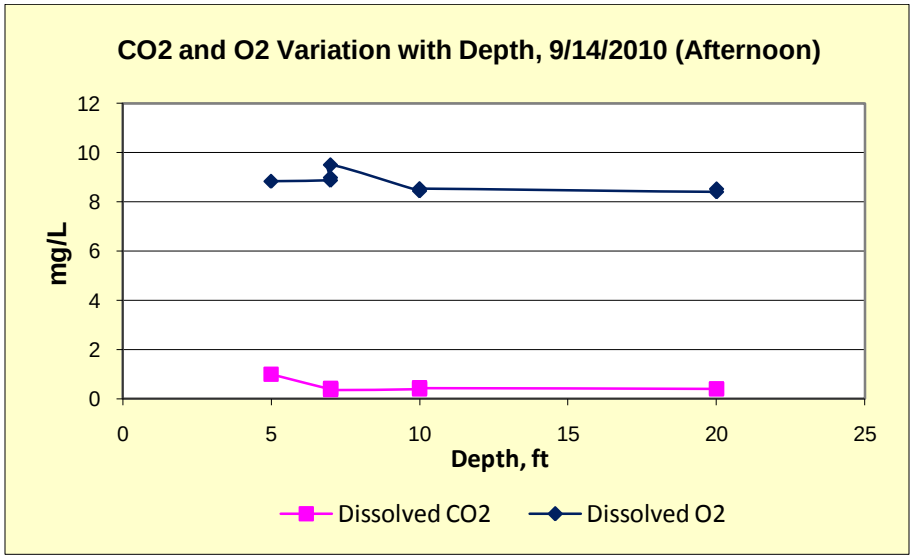

Figure 31

Figures 29-31. Inverse Relationship Between Aqueous Carbon Dioxide and Oxygen Levels, PM Samples.

Aqueous Carbon Dioxide Variation at Sampling Sites

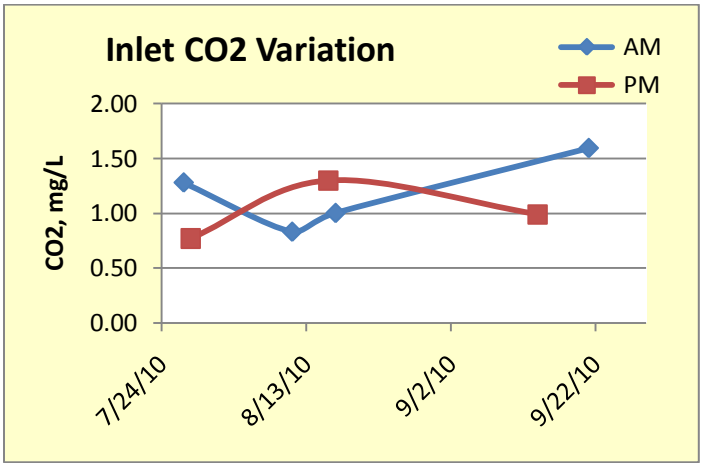

Figure 32

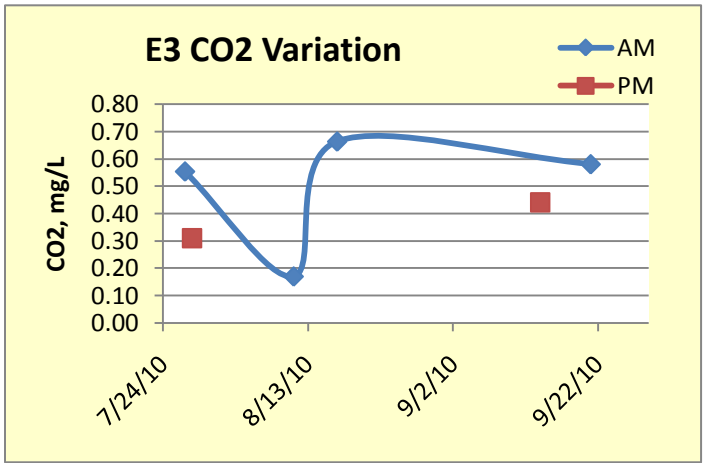

Figure 33

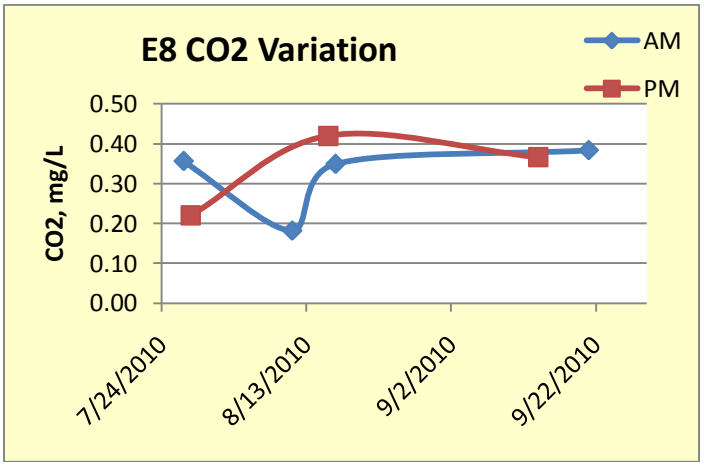

Figure 34

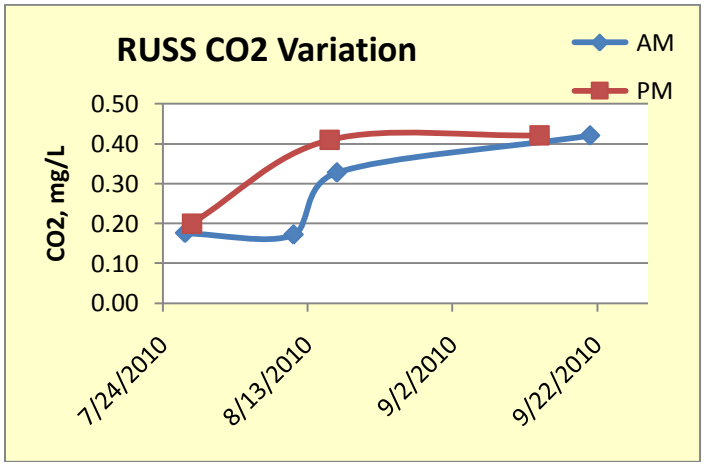

Figure 35

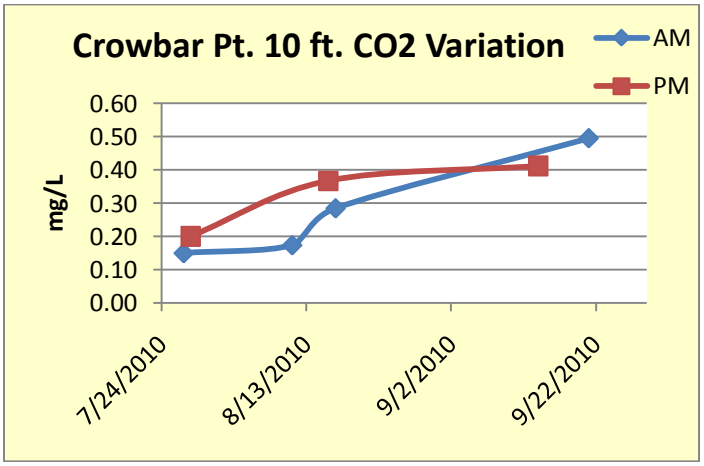

Figure 36

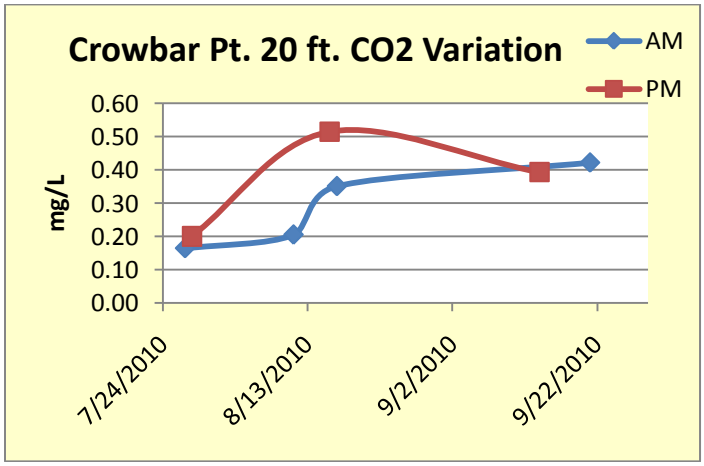

Figure 37

Figures 32-37. CO_2 variation at each sampling site, AM and PM composites.

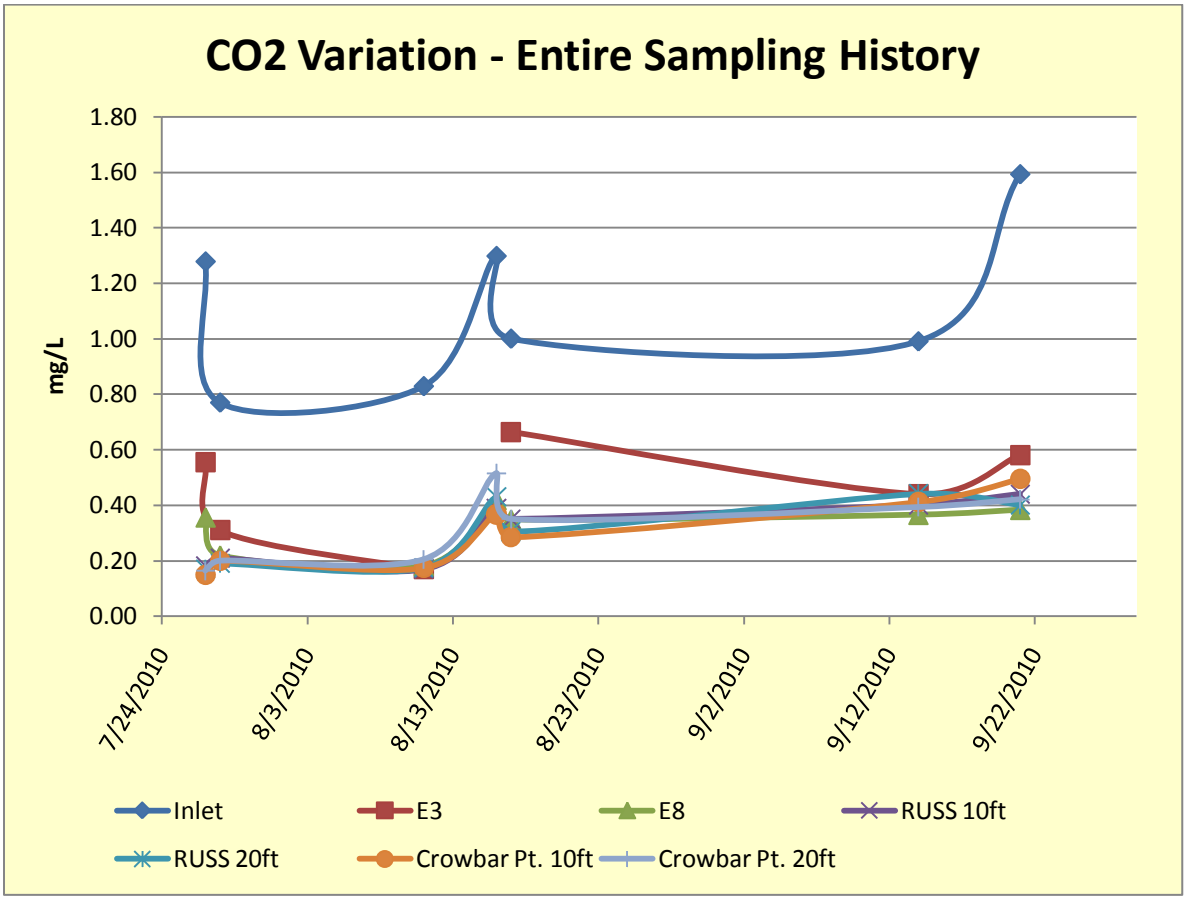

Figure 38

Figures 32-37 show the morning and afternoon carbon dioxide variations for each sampling site. The largest magnitude difference between AM and PM CO_2 concentrations appears to be in early August for all sites. It is striking that this difference shows the PM data as the higher CO_2 values; one would expect the highest carbon dioxide levels to be seen in the morning before sunrise because respiration produces CO_2 as a product, and this cannot be used until sunrise when photosynthesis resumes. This may be indicative of higher rates of respiration during the day, perhaps resulting from biomass decay towards the end of the season.

Figure 38 shows the carbon dioxide variation for the entire span of sampling. CO_2 levels were higher at the inlet for all sampling dates, both AM and PM. The inlet is shallow and this may be linked to higher productivity and therefore higher CO_2 levels in this location; sunlight penetrates sufficiently to the bottom of the inlet to allow the whole depth of water to be productive, and the inlet is shallow enough to allow submergent macrophytes to take root which would further affect carbon dioxide levels and productivity rates.

Aqueous Carbon Dioxide and Chlorophyll Variation with Depth

Carbon dioxide and chlorophyll concentrations showed quite similar depth distributions for most sampling dates. The highest concentrations for both parameters occur at shallow depths, dropping off steeply for depths below ~5ft. The distributions correlate poorly for the August 16-17 samples (Figures 47 and 50), possibly due to inaccurate measurements or a non-representative event of high productivity during this diel period (assumed to be non-representative because the other five sampling dates showed correlation of 0.75 or better in the CO_2-Chlorophyll analysis). The second point is missing on the August 16th CO_2 and chlorophyll graphs (Figures 45-46) because of failure to record data at the E3 sampling site.

Carbon dioxide is most likely highest near the surface due to diffusive effects from the atmosphere. The high concentrations of a carbon source and the high intensity of light near the surface are ideal conditions for growth, which is confirmed by the high chlorophyll values at this location. At deeper sampling sites, dissolved carbon dioxide and light intensity both decrease. This results in more sparse growth, as can be inferred from the declining chlorophyll values with increasing depths.

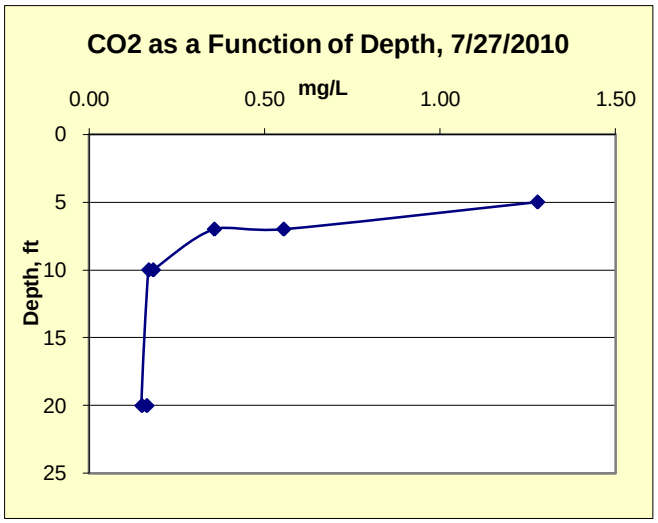

Figure 39

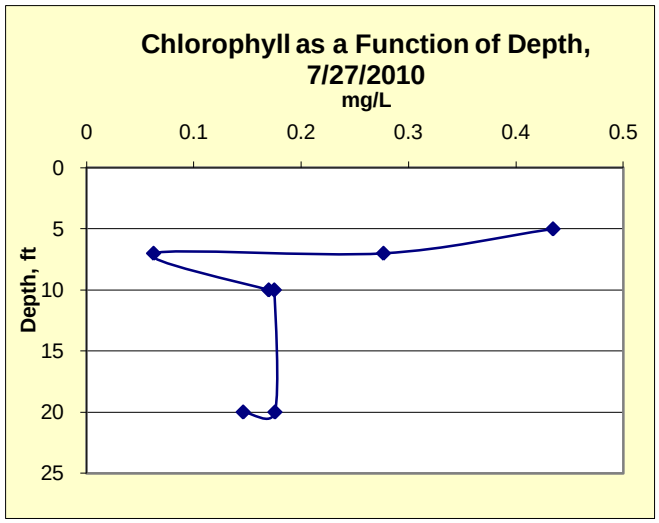

Figure 40

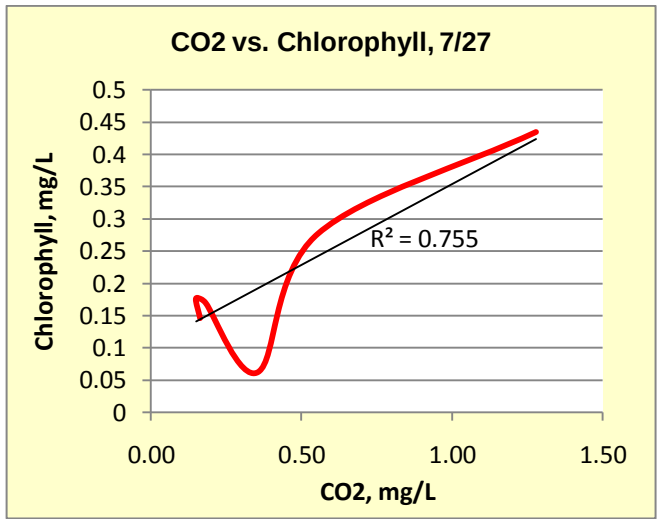

Figure 41

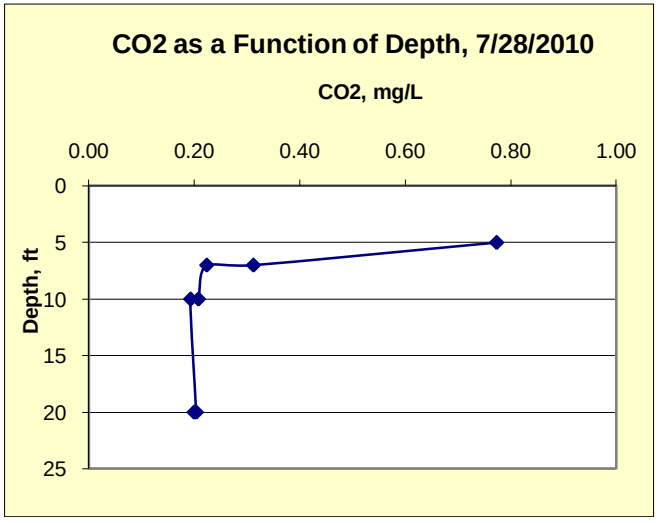

Figure 42

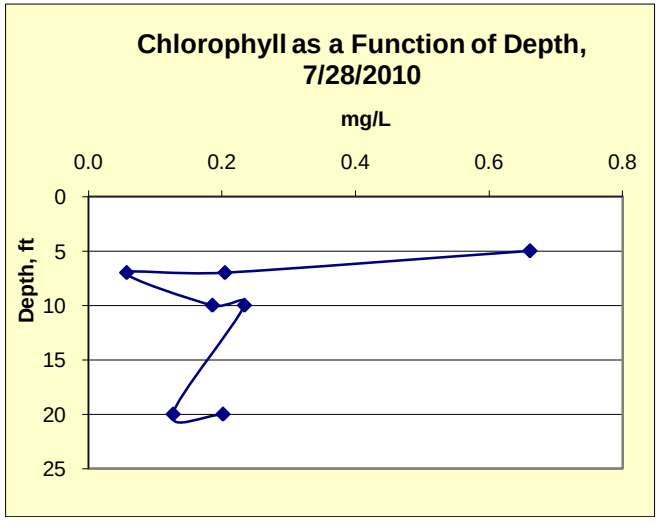

Figure 43

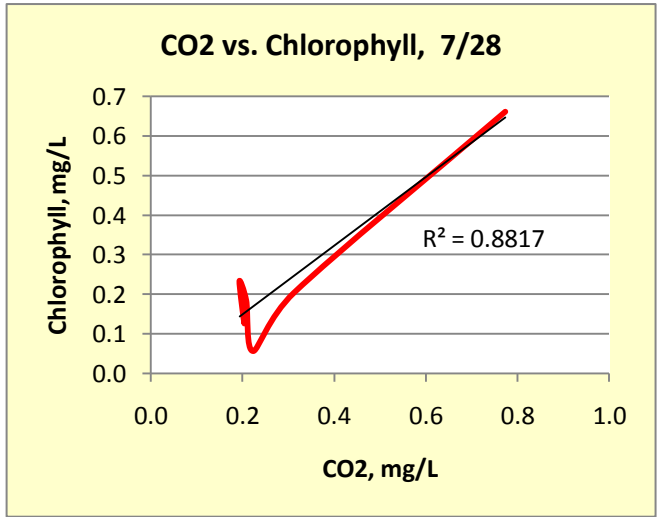

Figure 44

Figures 39-44. Correlations between CO2 and Chlorophyll concentrations for the first day/night pair (7/27 and 7/28).

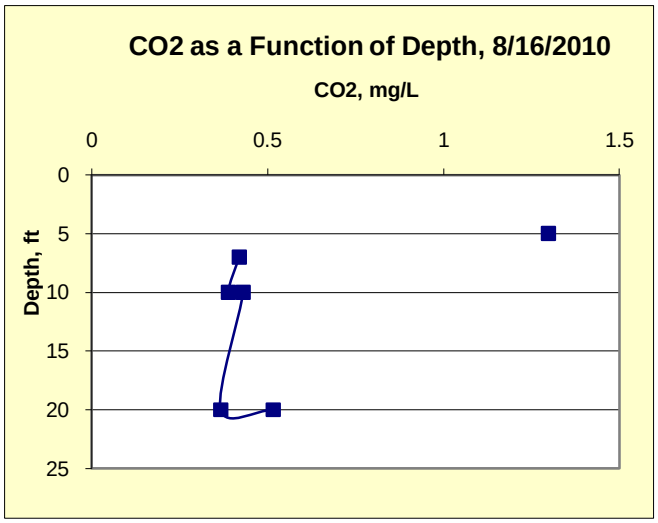

Figure 45

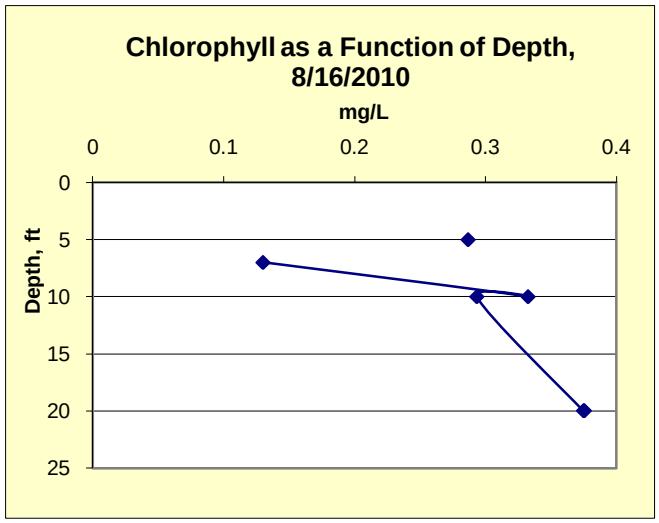

Figure 46

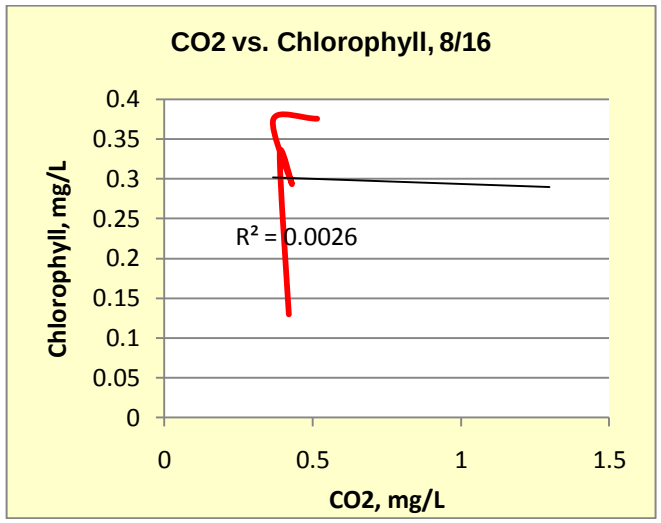

Figure 47

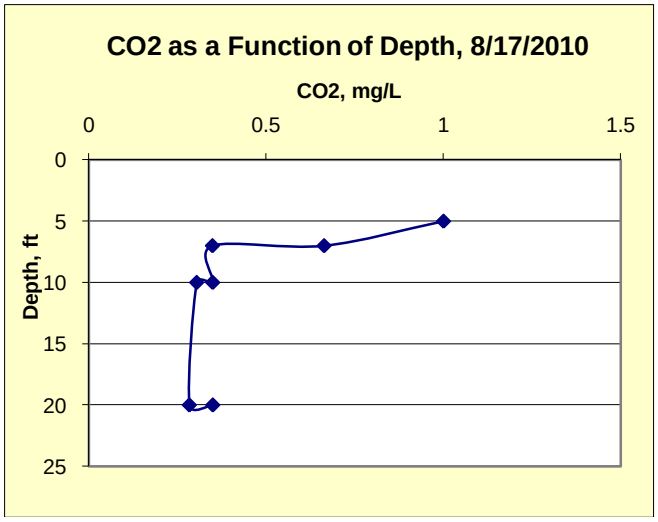

Figure 48

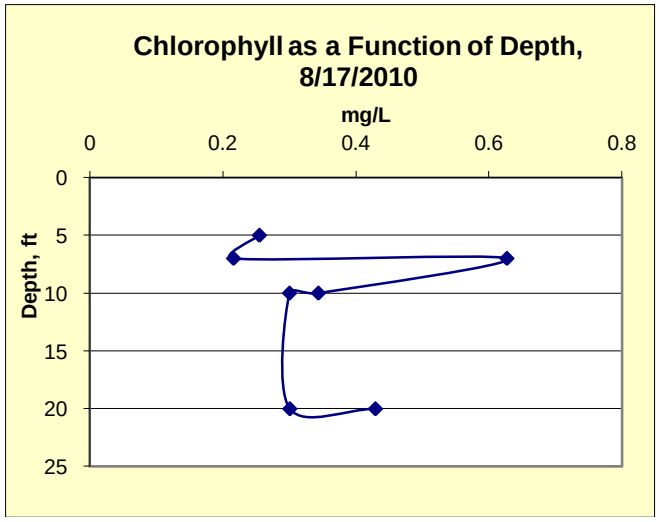

Figure 49

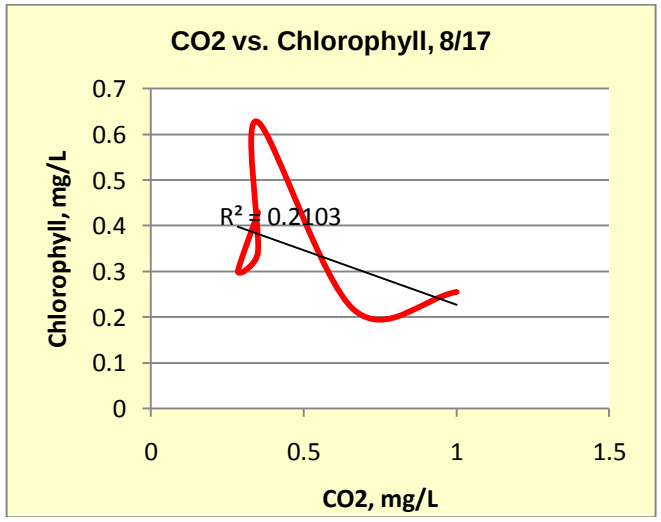

Figure 50

Figures 45-50. Correlations between CO2 and Chlorophyll concentrations for the second day/night pair (8/16 and 8/17).

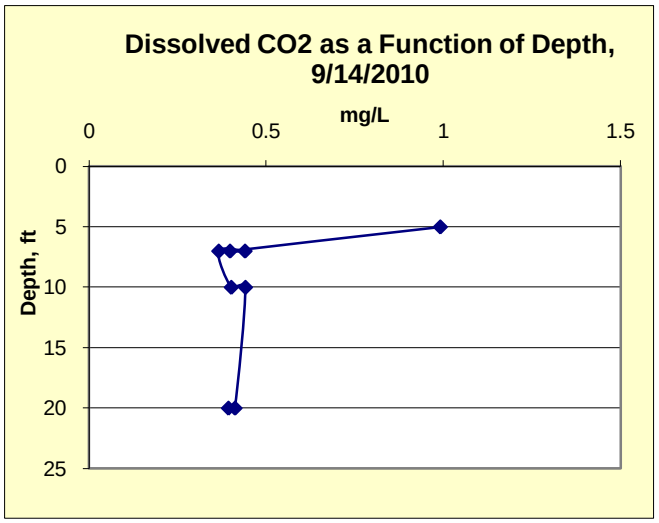

Figure 51

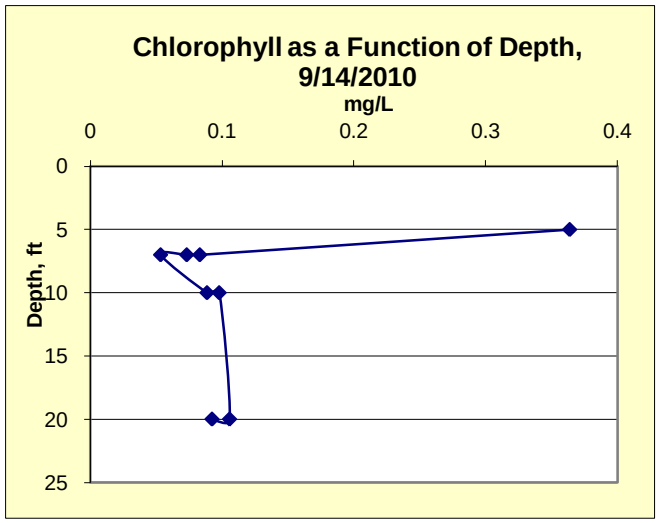

Figure 52

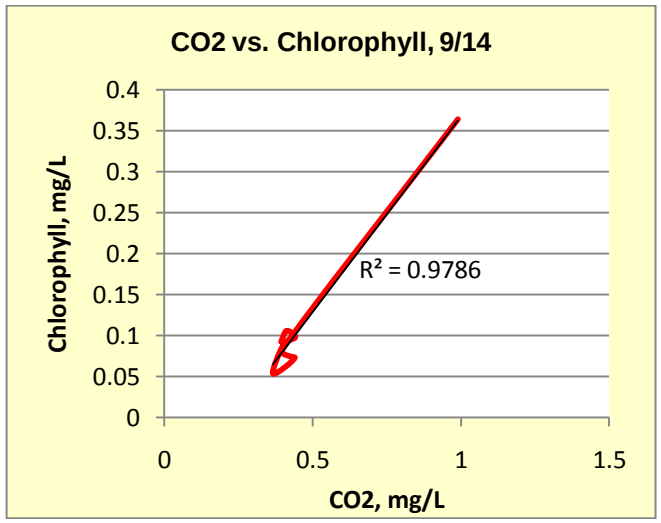

Figure 53

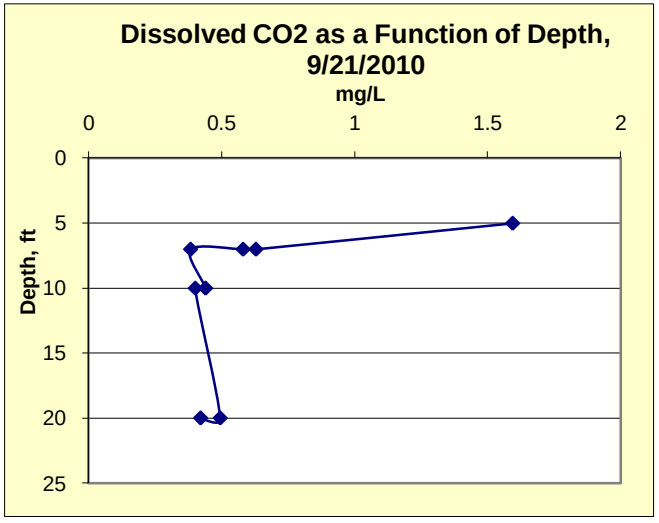

Figure 54

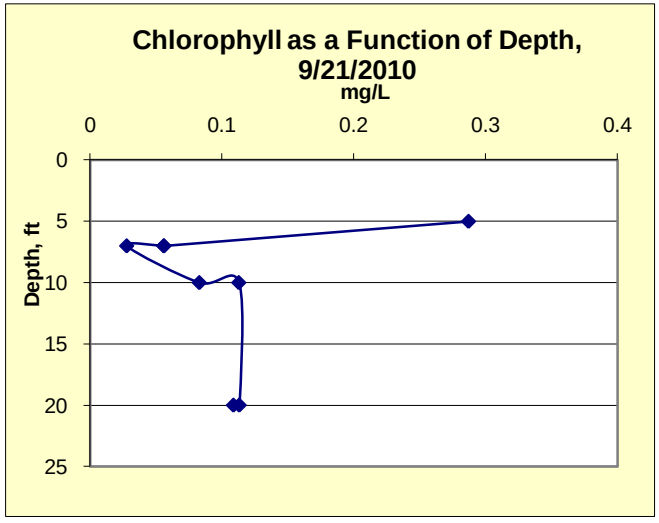

Figure 55

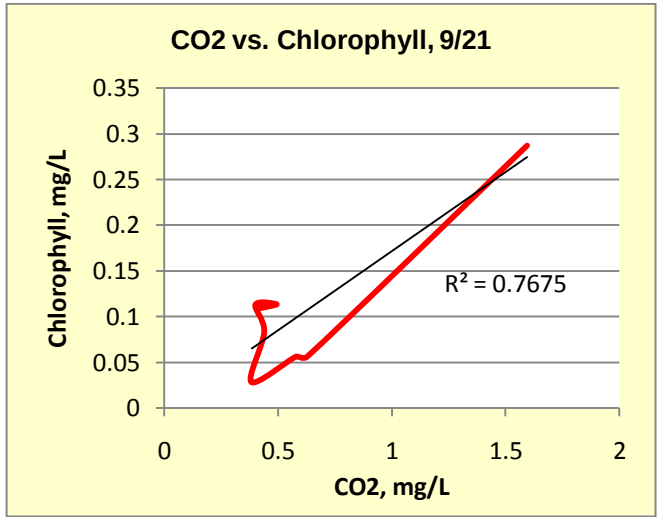

Figure 56

Figures 51-56. Correlations between CO2 and Chlorophyll concentrations for the third day/night pair (9/14and 9/21).

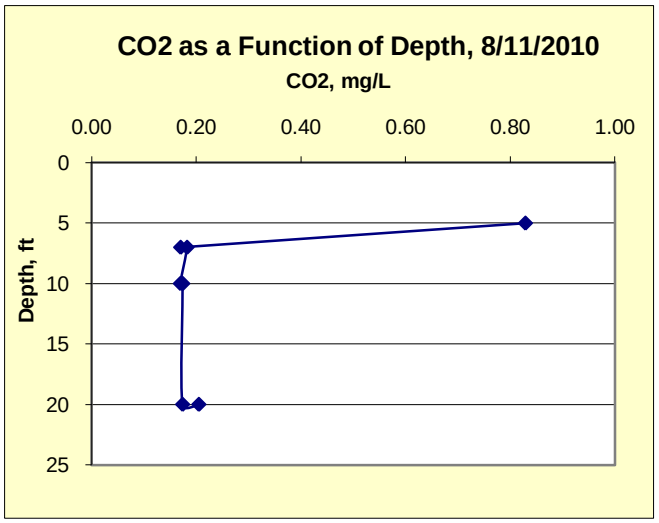

Figure 57

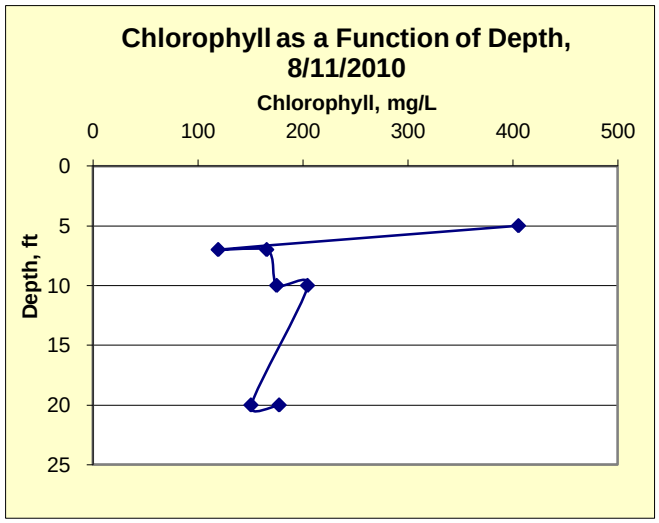

Figure 58

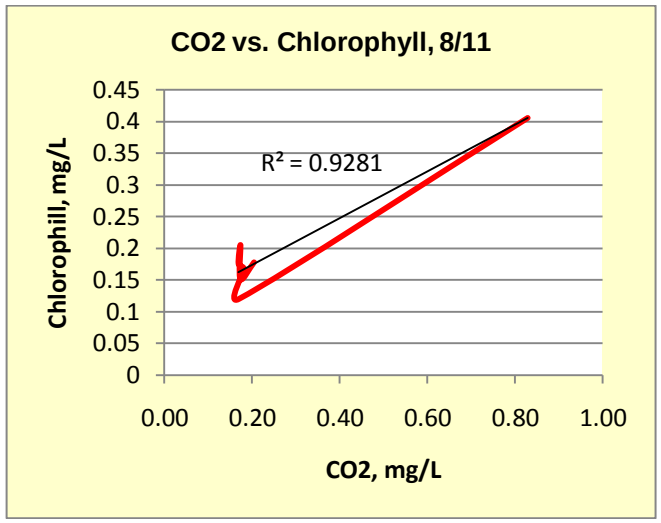

Figure 59

Figures 57-59. Correlations between CO2 and Chlorophyll concentrations for 8/11 (Morning sampling not associated with an afternoon day pairing).

4) Productivity Analysis

There are several standard methods for measurement of productivity. Light-dark bottle techniques have been widely used; the oxygen concentration difference between identical samples kept in different lighting is taken as a direct measure of productivity (Vollenwieder). This method is inappropriate for use in this study because it estimates productivity in a closed system that is much smaller than the lake ecosystem. Closed samples were taken at each site, but were only analyzed for carbonates in order to execute the dissolved carbon dioxide and alkalinity analyses. The bottle method was deemed unpractical for the estimating productivity in Cayuga Lake, as the samples are too small to be extrapolated as representative of the lake as a whole.

Oxygen deficit is another indirect way to measure productivity, applicable for lakes that exhibit stratification (Wetzel and Likens 1991). The oxygen lost from the hypolimnion during summer stratification can be used as a relative measure of productivity. The method calls for measuring the oxygen concentration in the hypolimnion on two dates, and the difference between these values is expressed as a rate of oxygen consumption per unit area of hypolimnetic surface. The hypolimnion is the lowest layer of a lake; in Cayuga Lake, the depth of the hypolimnion varies from ~10ft. in the inlet to more than 400ft. at the lowest depth. Sampling was limited to 20ft. and so this method is not directly applicable in this productivity estimation.

The difference in dissolved carbon dioxide concentrations between morning and afternoon samples of close-by sampling dates represents the total carbon uptake; in order to determine the productivity, we must account for energetic losses in the anabolism of complex molecules from CO_2. These net carbon dioxide differences can be used in comparison to oxygen fluctuations over the same periods in order to gain an understanding of CO_2/O_2 dynamics. Theoretically, we should see 1 mole of carbon dioxide consumed for every mole of oxygen:

$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$ (photosynthesis reaction)

The results of three methods to analyze productivity are presented below. The first method simply assumes the difference in diel CO_2 concentration is a measure of productivity. The second estimates net ecosystem productivity (NEP) by the difference in diel oxygen concentrations. The first two methods are compared to test the above hypothesis of a 1:1 CO_2/O_2 relationship. The last method is based on a carbon dioxide analysis that takes ammonium ion concentrations into account; this proved to be the simplest method and also best agreed with the carbon dioxide data.

Diel Carbon Dioxide Fluctuations

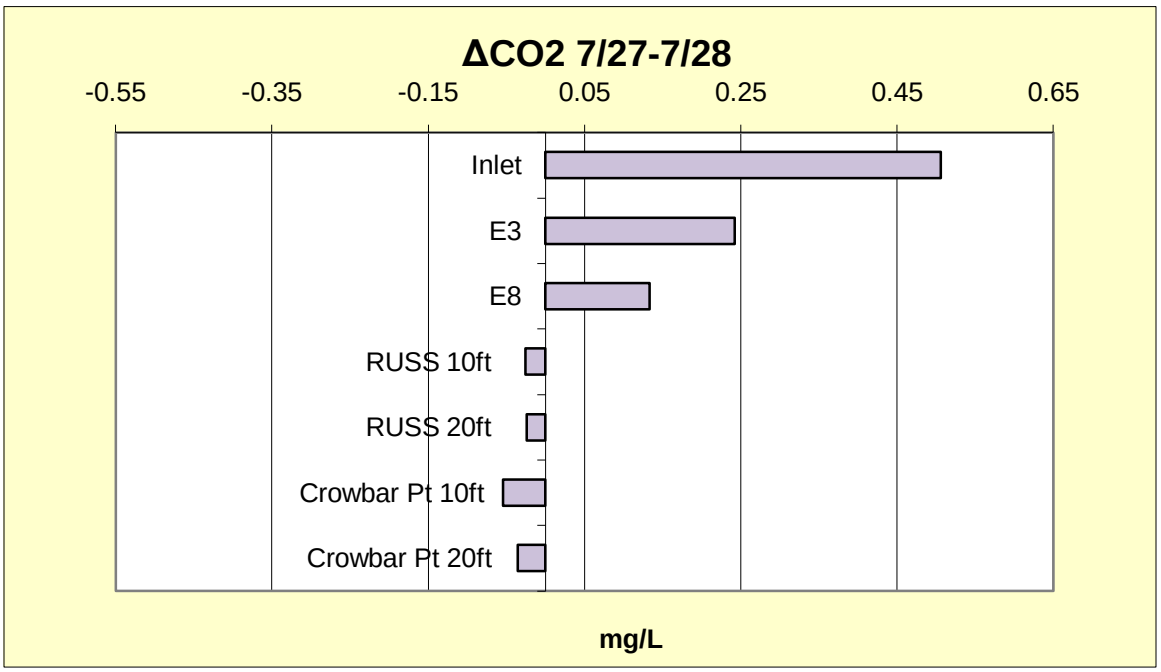

Figure 60

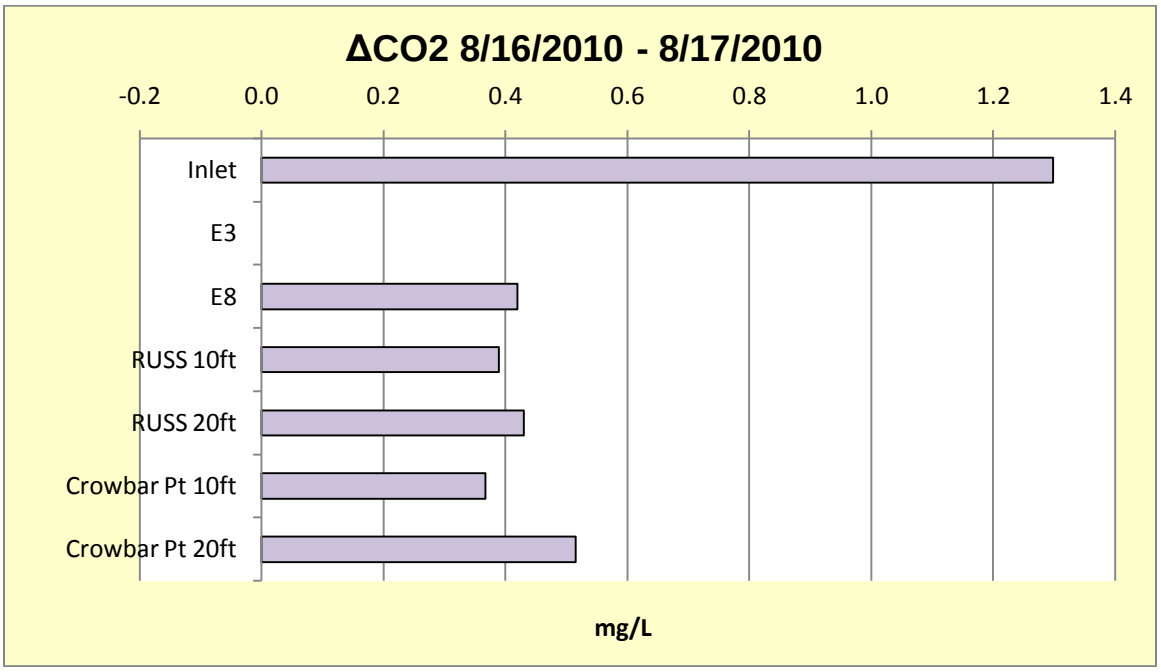

Figure 61

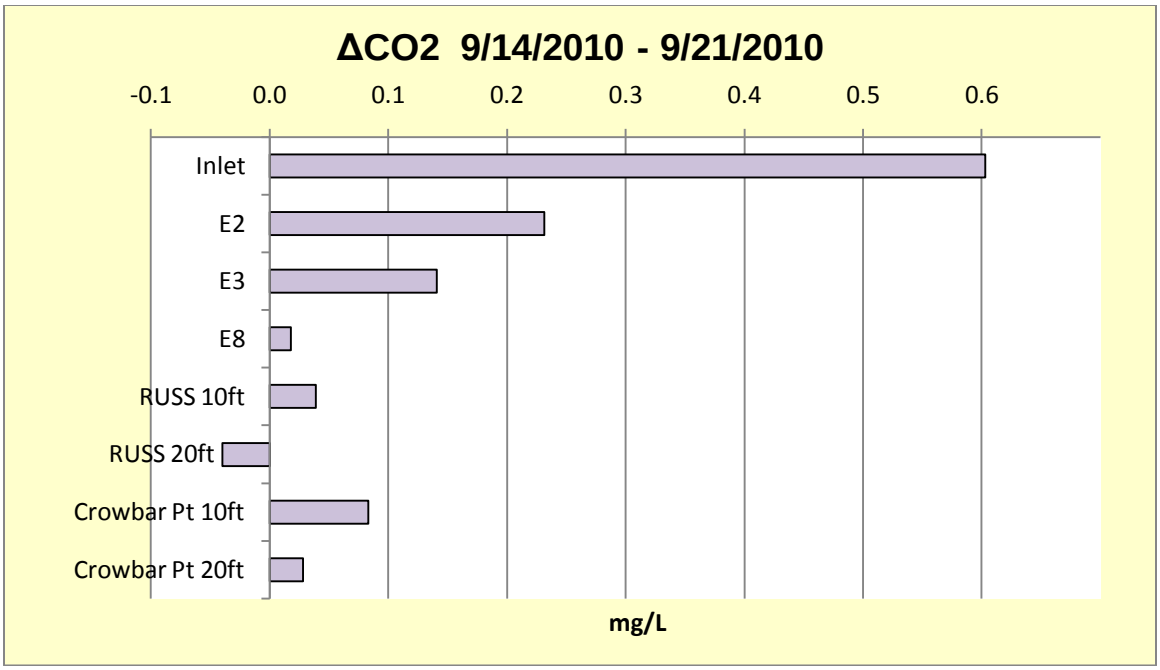

Figure 62

Diel carbon dioxide concentration differences were most pronounced at the inlet for all three day/night pairs. The inlet and Crowbar Point were the sampling locations furthest from the wastewater treatment plant's outfall, and so can serve as control points. Although the inlet does exhibit much higher productivity than any of the other sampling locations, this is most likely due to diffusive effects, as the inlet was the shallowest sampling depth and therefore most susceptible. Crowbar Point CO_2 fluctuations are relatively close in magnitude to those at the other locations; one can conclude that the outfall does not have significantly higher productivity than other parts of the lake.

Oxygen Concentration Variation

Productivity estimation by oxygen analysis proved to be extremely biased toward atmospheric diffusion at the surface. As can be seen from figures 63-65, NEP has a much higher magnitude at the surface locations than at deeper locations; this is because the diffusive term was more significant than the measured difference in oxygen concentrations at depths below the surface.

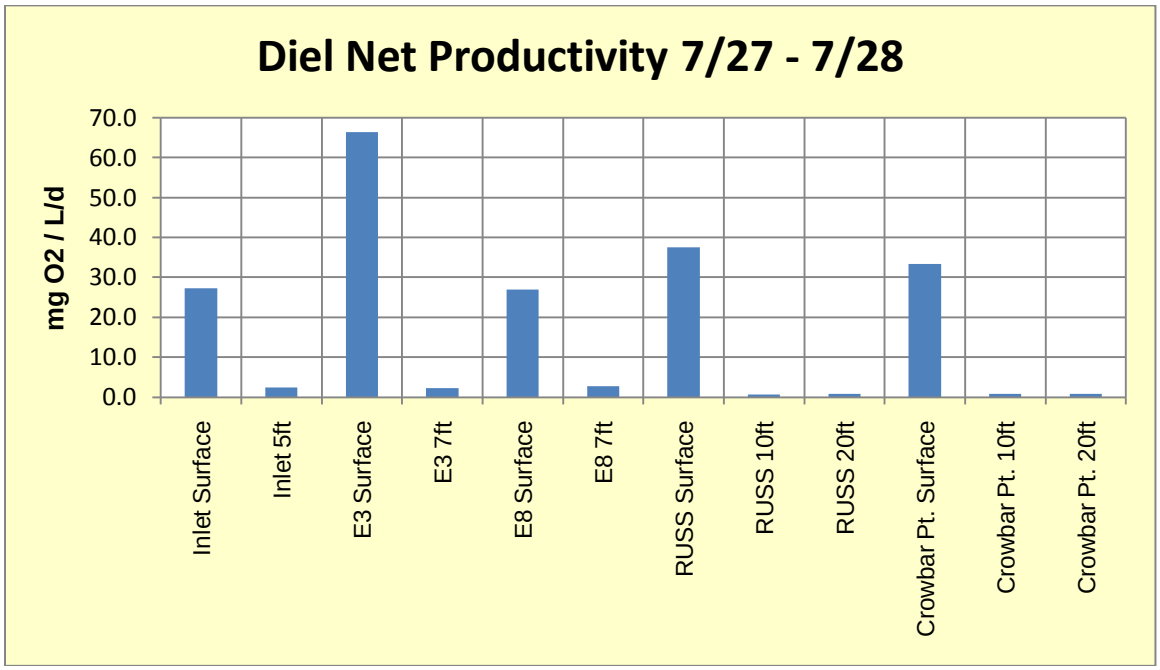

Figure 63

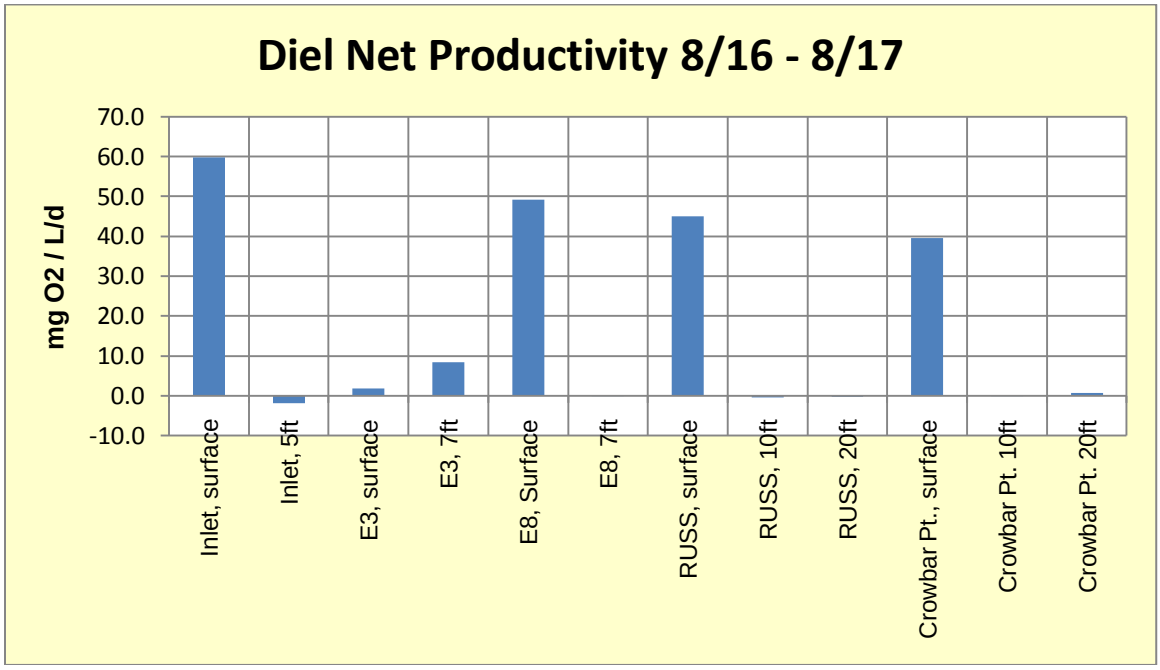

Figure 64

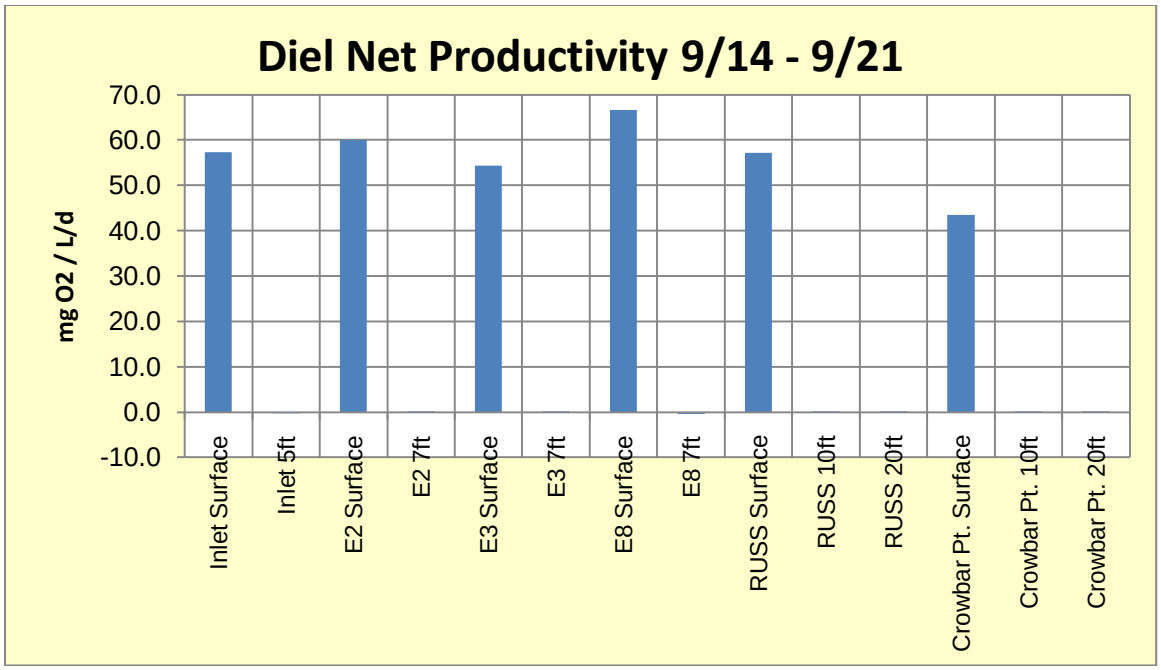

Figure 65

Surface Effects

When represented by Figures 63-65, productivity is seemingly highly variable. It is the surface measurements, however, that are most productive when productivity is represented as the diel difference in oxygen concentrations. These high values are not representative of the lake as a whole, as can be seen from the drastically lower NEP values found at depths below the surface. Even the inlet, which had the shallowest sampling depth (5ft) shows productivity values radically different from the surface productivities. This method of calculating productivity (see Methods, p.10) takes into account diffusion at the surface due to wind effects. These are assumed to act only at the surface, and they proved significant; productivities at depths below the surface are presented as simply the difference in dissolved oxygen concentrations in the day/night pairs because wind effects would not be significant at these depths. Diffusion due to wind provided an influx of oxygen much greater than the magnitude of concentration change at lower depths, and so the lake surface is found to be the most productive depth. This can be backed by the theory that shallow depths will receive a higher percentage of light irradiance and therefore will be more hospitable to growth, but irradiance measurements were beyond the scope of this project.

When one considers NEP at depths below the surface, the productivity is apparently much lower in magnitude. One thing to note is that the values do not vary very much at different sampling locations. Again, the inlet and Crowbar Point are the furthest sampling locations away from the wastewater treatment plant's outfall location and can be considered control locations – if productivity values were considerably different at the inlet and Crowbar Point sites, we could reasonably deduce that the wastewater outfall has an effect on productivity at proximate sampling points (E2, E3, E8, RUSS). This is not the case. Although there is some variation between sampling dates, it is not of a large magnitude and there exists a relative homogeneity in magnitudes of productivity at all sampling points below the surface; one can infer that the

wastewater outfall has no significant influence on productivity because the proximate sampling points do not show significantly higher NEP than the control sites (Inlet and Crowbar Point) for any of the day/night pairs (Figures 66-68).

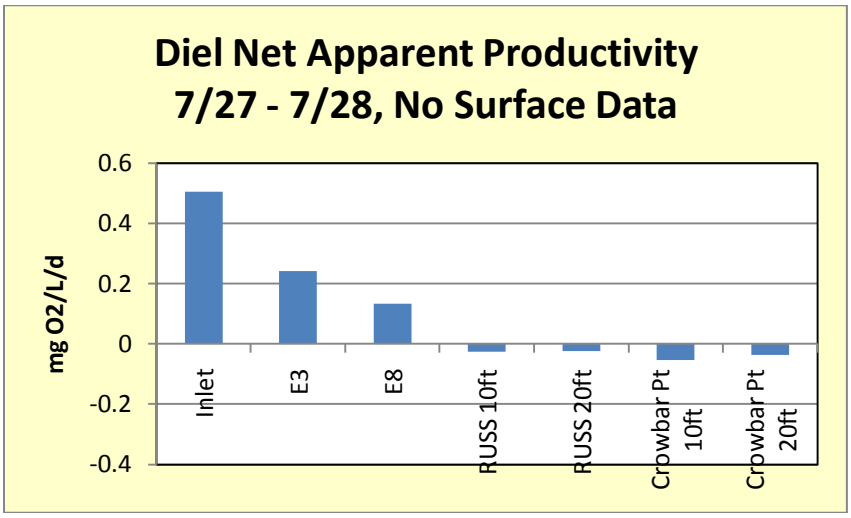

Figure 66

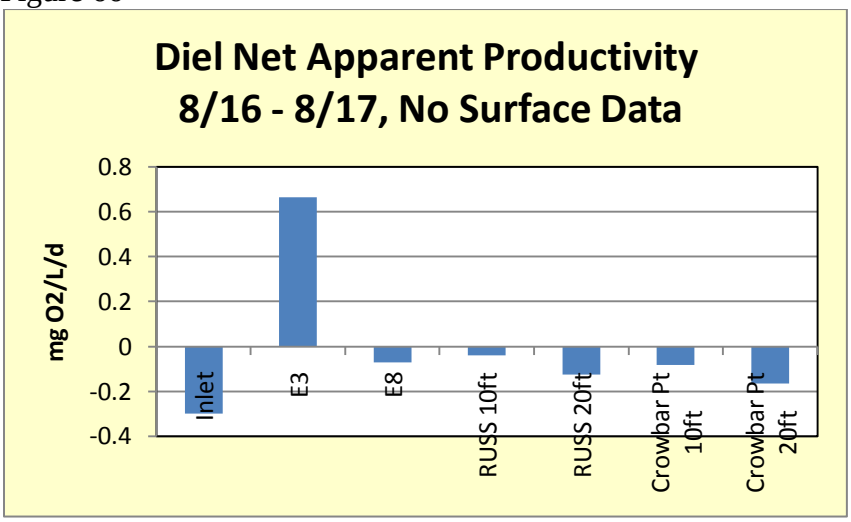

Figure 67

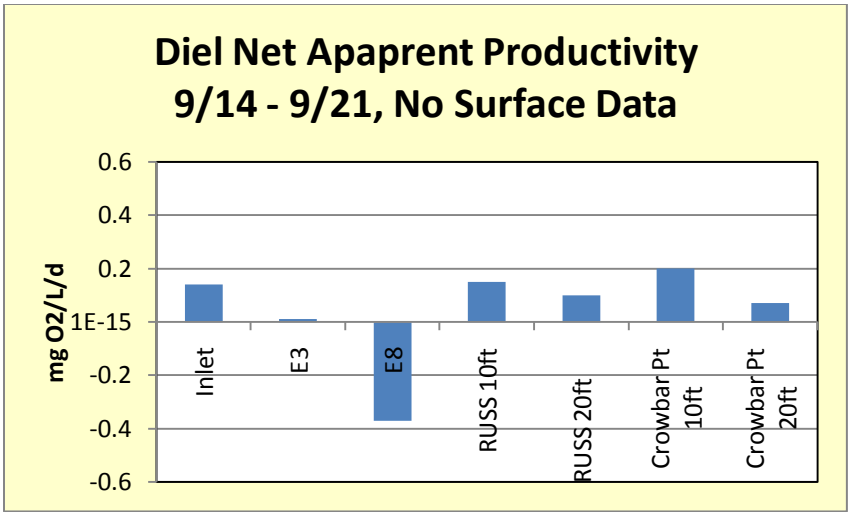

Figure 68

Net Apparent Productivity with Carbon Dioxide Fluctuation

In order to gain a better understanding of the relationship between productivity and carbon dioxide concentration, NEP was plotted against the concentration difference of CO_2 for the three day/night pairs. Again, surface data is not included in this analysis because it proved to be very biased towards atmospheric diffusion. The correlation increased as the summer progressed, but even the weakest correlation of 0.62 (Figure 69) shows a positive relationship.

Net ecosystem productivity was calculated as the oxygen concentration change in the two closest day/night sampling pairs. Comparing these values with the changes in CO_2 concentrations on a molar basis did not result in a 1:1 relationship, as expected from the stoichiometry of photosynthesis ($6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$). In reality, the relationship is nowhere near this ideal and varies from 8, 15.5, and 147 moles of oxygen per mole of carbon dioxide for the day-night pairs of July 27-28, August 16-17, and September 14-21 respectively. There is, however, a strong correlation between NEP and CO_2 for the August and September day/night pairs.

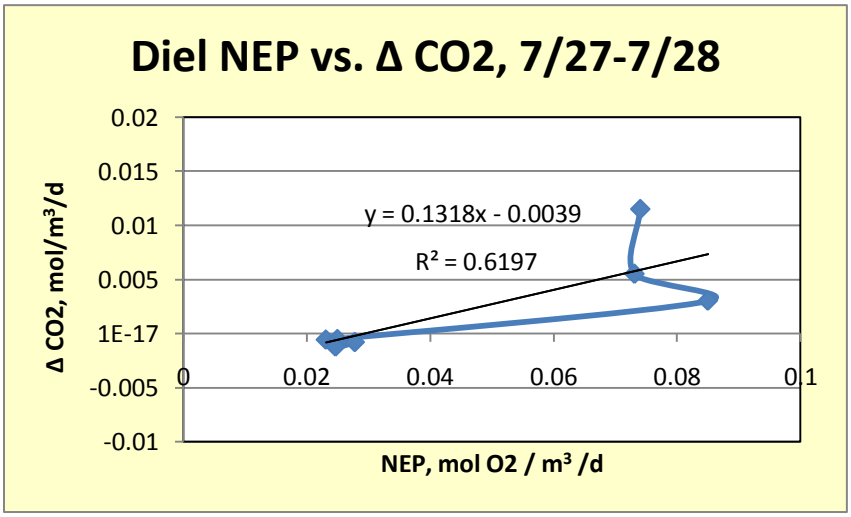

Figure 69

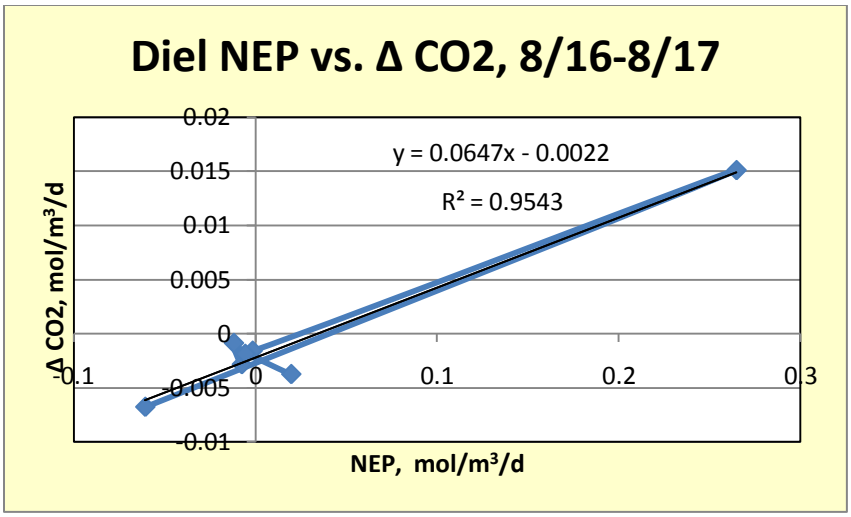

Figure 70

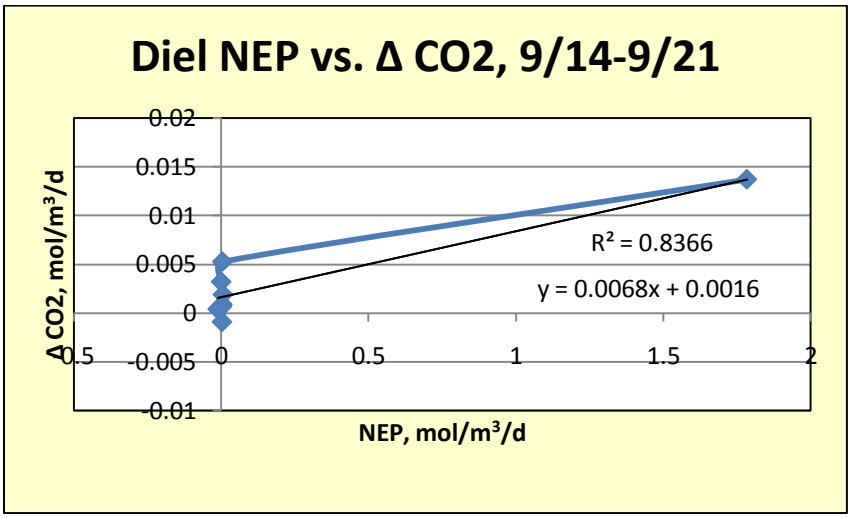

Figure 71

Carbon Dioxide Metabolism Model

One of the main aims of the study was to arrive at a simple, directly applicable relationship to estimate productivity based on carbon dioxide concentration. In addition to using standard methods of dissolved oxygen analysis to estimate production, the method first presented by Ohle in 1956 was used as basis for analyzing productivity based on carbon dioxide fluctuations. The detailed methodology is presented in Appendix 2. The method takes into account carbon that may be bound in the NH_4HCO_3 compound; it proved extremely promising, with the carbon dioxide data for every day/night pair agreeing at 98% or better with this established carbon dioxide method (Figures 73-75).

The method does not give a 1:1 correlation of CO_2 magnitudes; the data taken with the dissolved CO_2 meter is usually at least two times as great as the calculated metabolism values, but the equations governing the relationship are similar in all three instances. This is probably due to the fact that the dissolved CO_2 meter measures total carbonates when the sample is treated with acid, while the metabolism estimate uses ammonium ion concentration to estimate the bicarbonate concentration; this is likely an under-estimate because Cayuga Lake has a pH of ~8, and most carbonates are present in the bicarbonate form.

This method will prove highly useful, as the reading taken by the dissolved CO_2 analyzer can be used directly in a simple equation that estimates productivity. The composite model is given below (Figure 72); it is based on a locational average of the data for individual day/night pairs given in Figures 73-75.

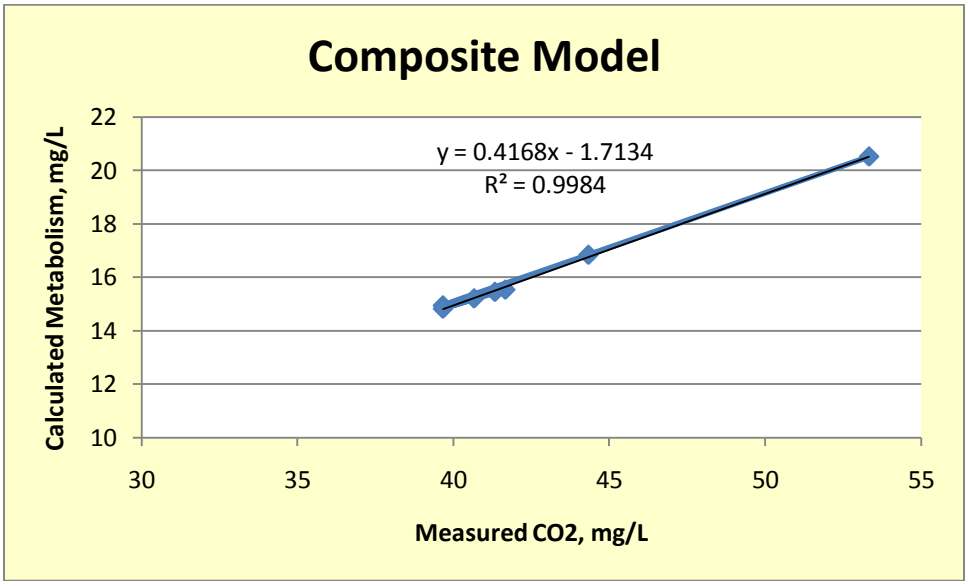

Figure 72

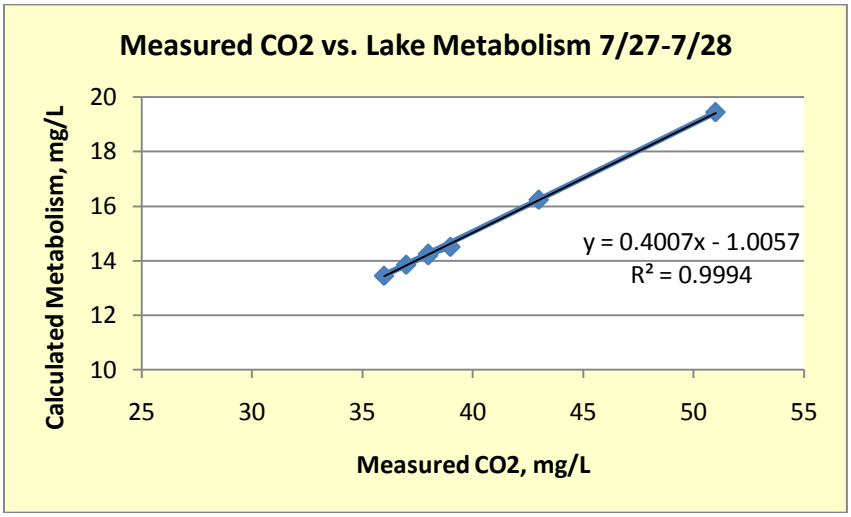

Figure 73

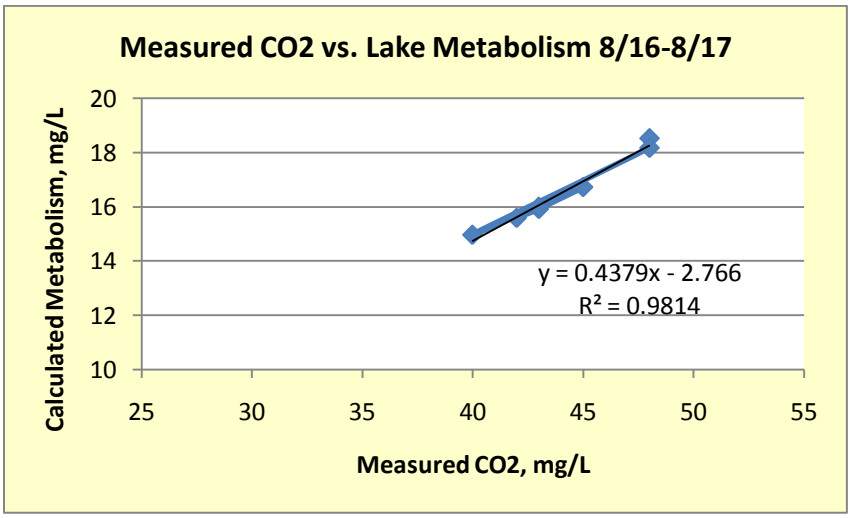

Figure 74

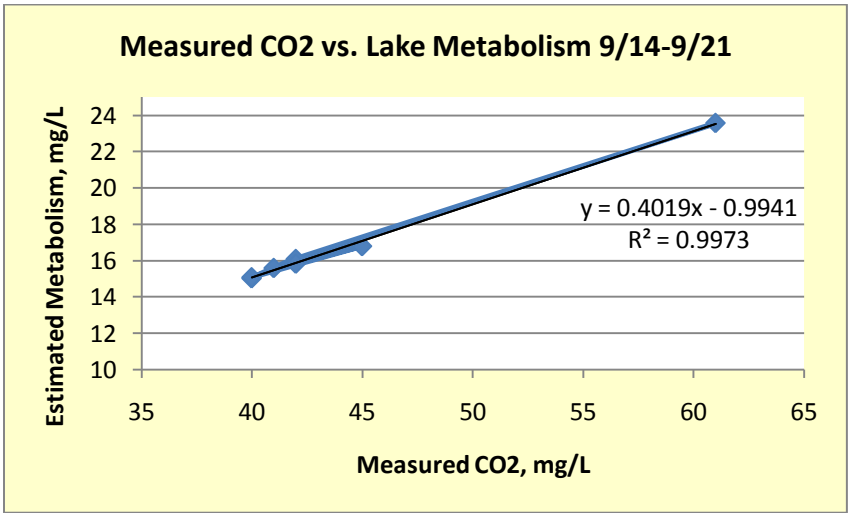

Figure 75

5) Conclusions

The main points of interest in this study are thus summarized:

1) Titration and mathematical analysis yielded similar values for the dissolved carbon dioxide and alkalinity measurements, granting credibility to using the OxyGuard dissolved CO_2 meter in productivity analysis.

2) An inverse relationship exists between dissolved carbon dioxide and oxygen levels at shallow depths, where most photosynthetic activity occurs. The concentrations of these parameters stagnate with increasing depth.

3) Dissolved carbon dioxide represents only a tiny fraction of carbonates in Cayuga Lake. Most carbonates are present in the HCO_3^- (bicarbonate) form due to the lake's slightly basic pH.

4) Carbon dioxide levels vary throughout the diel period as well as through longer (seasonal) time periods.

5) Carbon dioxide and chlorophyll concentrations show similar distribution, with the highest values seen near the lake surface – presumably due to more intense light penetration at shallower depths.

6) Productivity analysis based on oxygen concentrations was highly influenced by surface diffusive effects.

7) Oxygen and dissolved carbon dioxide comparisons compare well, when surface effects are ignored.

8) The model presented by Ohle and adapted by Wetzel and Likens strongly agreed with measured CO_2 concentrations. Of the three methods for productivity estimation, this is the most useful because the CO_2 readings can be used directly from the OxyGuard CO_2 analyzer – although these values are a measure of total carbonates, there is no need to find the fraction of carbon dioxide.

6) Future Analysis

The model developed is promising because of its simplicity and direct usability – no need to find the actual carbon dioxide concentration based on the total carbonates reading given by the OxyGuard meter. However, it is based on only six sampling days' worth of data. The sampling season in Ithaca is roughly April-October, depending on weather, and the season ended before more data could be gathered. When the new season begins in spring 2011, additional data will prove useful in making the model more robust.

Appendix I: Carbonate System Equilibria

Mass Balance $C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$ (eq. 1)

Charge Balance $[H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$ (eq. 2)

Equilibria $H_2O \leftrightarrow [H^+] + [OH^-]$ (eq. 3)

The rate of this reaction is governed by the dissociation constant of water, K_w:

$K_w = [H^+][OH^-] = 10^{-14}$ (eq. 4)

Similarly,

$[H_2CO_3^*] \leftrightarrow [H^+] + [HCO_3^-]$, governed by K_1. (eq. 5)

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} = 10^{-6.35} \quad \text{(eq. 6)}$$

And

$[HCO_3^-] \leftrightarrow [H^+] + [CO_3^{2-}]$, governed by K_2. (eq. 7)

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 10^{-10.33} \quad \text{(eq. 8)}$$

By manipulating the above dissociation constants, we get expressions for bicarbonate and carbonate concentrations.

From eq.6 for K_1,

$$[HCO_3^-] = \frac{K_1[H_2CO_3^*]}{[H^+]} \quad \text{(eq. 9)}$$

From eq. 8 for K_2 and eq. 9,

$$[CO_3^{2-}] = \frac{K_2[HCO_3^-]}{[H^+]} = \frac{K_1K_2[H_2CO_3^*]}{[H^+]^2} \quad \text{(eq. 10)}$$

Therefore we arrive at a useful expression for total carbonates in terms of dissociation constants by combining eq.s 1, 9, and 10:

$$C_T = [H_2CO_3^*]\left[1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right] \quad \text{(eq. 11)}$$

It is practical to represent the species of the carbonate system as fractions of C_T. These fractions are represented as α values. For diprotic acids these values, also called distribution coefficients, are as follows:

$$\alpha_o = \frac{[H_2CO_3^*]}{C_T}$$, the fraction of carbonates present as $[H_2CO_3^*]$ (eq. 12)

From eq. 11 above,

$$\alpha_o = \left[1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right]^{-1} \quad \text{(eq. 13)}$$

Similarly, α_1 represents the fraction of carbonates present as $[HCO_3^-]$ and α_2 the fraction present as $[CO_3^{2-}]$.

$$\alpha_1 = \left[1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]}\right]^{-1} \quad \text{(eq. 14)}$$

$$\alpha_2 = \left[1 + \frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2}\right]^{-1} \quad \text{(eq. 15)}$$

In open systems such as Cayuga Lake, the $CO_{2\,(aq)}$ levels (and therefore aqueous $H_2CO_3^*$ levels) cannot be assumed to be constant because some fraction may volatilize to the atmosphere. We employ Henry's Law to account for this disparity.

$$[H_2CO_3^*] = K_H P_{CO2} = C_T \alpha_o \quad \text{(eq. 16)}$$

where K_H is the Henry's Law constant for CO_2 and P_{CO2} represents the partial pressure of CO_2 in the gaseous phase.

From the above,

$$C_T = \frac{K_H P_{CO2}}{\alpha_o} \qquad \text{(open systems)} \quad \text{(eq. 17)}$$

Alkalinity

Alkalinity corresponds to a water's ability to neutralize acid. Due to ionization, the carbonate system species have different contributions to alkalinity. $H_2CO_3^*$ is a neutral species and does not contribute to alkalinity. Bicarbonate can neutralize one equivalent of protons, and carbonate can neutralize two. The dissociation products of water, H^+ and OH^-, also contribute to alkalinity. Therefore,

$$Alk = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \quad \text{(eq. 18)}$$

Combining eq.s 4, 14, 15, and 18,

$$Alk = C_T\left(\alpha_1 + 2\alpha_2\right) + \frac{K_w}{[H^+]} - [H^+] \quad \text{(eq. 19)}$$

In open systems, from eq. 17,

$$Alk = \frac{K_H P_{CO2}}{\alpha_o}\left(\alpha_1 + 2\alpha_2\right) + \frac{K_w}{[H^+]} - [H^+] \quad \text{(eq. 20)}$$

Appendix II. Productivity Estimate Method Using Carbon Dioxide Summation

(Adapted from Wetzel and Likens 1991)

Layer	β 3.38*NH_4	b 0.721*β	α HCO_3^-	x α-β	a 0.3605*x	c CO_2	∑CO_2 a + b + c
Surface - 5ft							
E3 7ft							
E8 7ft							
RUSS 10ft							
RUSS 20ft							
Crowbar Pt. 10ft							
Crowbar Pt. 20ft							

The following assumptions apply to the method:

a) The molecular ratio of ammonium bicarbonate NH_4^+: HCO_3^- = 18.04:61.02. Then bicarbonate in ammonium bicarbonate is estimated as

$$HCO_3^- = \frac{\quad}{\quad} = 3.38*NH_4^+ = \beta$$

b) The molecular ratio of HCO_3:CO_2 = 61.02:44.01. Then the CO_2 of bicarbonate of the ammonium bicarbonate is

$$CO_2 = \frac{\quad}{\quad} = 0.721*\ HCO_3^- = 0.721*\ \beta = b$$

c) The measured concentration of HCO_3^- in mg/L is represented as α.

d) x = α – β removes the error of bicarbonate from NH_4HCO_3.

e) Now one converts the total bicarbonate to CO_2. Half is bound as CO_2 of $CaCO_3$.

$$a = \frac{\quad}{\quad} = 0.3605*x$$

f) The measured concentration of free carbon dioxide in mg/L is represented by c.

g) The total corrected carbon dioxide is an estimate of lake metabolism.

$$\sum CO_2 = a + b + c$$

Appendix III. Sample calculations for titrations and mathematical analysis. This uses data from 7/27/2010. All other data was manipulated similarly.

Location	Depth, ft	Time	CO2, mg/L	pH (Boat)	pH (Hydrolab)	Patm, mmHg	Patm, atm	PCO2, atm		
Inlet	5	5:31 AM	60	3	7.96	765.3	1.006973684	0.000332301	mmHg/atm	760
E3	7	5:52 AM	46	3	8.21	765.3	1.006973684	0.000332301	%CO2 in air	0.033
E8	7	6:04 AM	39	3	8.33	765.4	1.007105263	0.000332345		
RUSS	10	6:27 AM	40	3	8.63	765.5	1.007236842	0.000332388		
RUSS	20	6:22 AM	37	3	8.65	765.3	1.006973684	0.000332301		
Crowbar Pt	10	6:55 AM	39	3	8.68	765.35	1.007039474	0.000332323		
Crowbar Pt	20	6:49 AM	36	3	8.63	765.3	1.006973684	0.000332301		

Titrations

Phenolphthalein	CO2, mg/L	Phenolphtalein	Bromcresol Green			Phenolphthalein Alk	Methyl Orange Alk	Carbonate	Bicarbonate	Alkalinity
NaOH, mL		H2SO4, mL	H2SO4, mL	P	T	ppm as CaCO3	ppm as CaCO3	2Px10, ppm	(T-2P)x10, ppm	mg/L as CaCO3
0.18	1.8	0	14.47	0	14.47	0	144.7	0	144.7	144.7
0.15	1.5	0	11.52	0	11.52	0	115.2	0	115.2	115.2
0.06	0.6	0	9.84	0	9.84	0	98.4	0	98.4	98.4
0	0	0.64	9.64	0.64	10.28	6.4	96.4	12.8	90	102.8
0	0	0.57	9.71	0.57	10.28	5.7	97.1	11.4	91.4	102.8
0	0	0.51	9.82	0.51	10.33	5.1	98.2	10.2	93.1	103.3
0	0	0.56	9.93	0.56	10.49	5.6	99.3	11.2	93.7	104.9

Accounting for HCO3- converted to CO2

pH	7.96	Kw	1E-14	
[H+]	1.09648E-08	KH	0.034	mol/Latm
K1	5.01187E-07	PCO2	0.000332301	atm
K2	5.01187E-11	MW CO2	44000	mg/mol
		MW CaCO3	100000	mg/mol
alpha 0	0.021313896			
alpha 1	0.974233			
alpha 2	0.004453104			
sum	1			

Theoretical CO2 Concentrations & Alkalinity

Depth, ft	CO2, mg/L	pH	alpha 0	CT, M	Dissolved CO2	alpha 1	alpha 2	Alkalinity, M	Alkalinity	LDO
					mg/L				mg/L as CaCO3	mg/L
5	60	7.96	0.021314	0.001363636	1.28	0.974233	0.004453	0.001342	134.15	7.08
7	46	8.21	0.012056	0.001045455	0.55	0.979978	0.007966	0.001043	104.28	7.91
7	39	8.33	0.009149	0.000886364	0.36	0.980346	0.010505	0.000890	88.97	7.72
10	40	8.63	0.004559	0.000909091	0.18	0.974605	0.020837	0.000928	92.82	9.21
10	39	8.65	0.004350	0.000886364	0.17	0.973848	0.021802	0.000906	90.63	9.19
20	37	8.68	0.004055	0.000840909	0.15	0.972614	0.023331	0.000862	86.19	9.19
20	36	8.63	0.004559	0.000818182	0.16	0.974605	0.020837	0.000836	83.58	9.14

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